A COMPREHENSIVE MECHANISM FOR ANTHRAQUINONE MASS TRANSFER IN ALKALINE PULPING

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A COMPREHENSIVE MECHANISM FOR ANTHRAQUINONE MASS TRANSFER IN ALKALINE PULPING

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For my daughter Kaelynn,
who has shown me what it truly means
to have heart.

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SUMMARY

A mechanism for the mass transfer of anthraquinone (AQ) into wood during alkaline pulping has been developed. Although the chemistry of action of AQ is well-developed, there has not been much work conducted on its diffusion properties. These are important because AQ is insoluble in pulping liquors. There must be a phase change due to chemical reaction for any diffusion of AQ species.

Several researchers have reported interesting effects when using AQ. The discrepancies between different experiments with AQ indicate that something other than the chemistry is at work. Because most of the differences arise from variations in pulping conditions, it is likely that mass transfer is the source of these discrepancies.

A model system was therefore developed to explore the mass transfer properties of AQ. It was shown that AQ must be reduced to anthrahydroquinone (AHQ) before any permeation of a membrane can occur. However, if the reduction is done in the bulk solution, permeation still does not happen at normal concentrations. Only at very high concentrations can bulk reduction achieve membrane permeation for AQ. It is only when AQ is reduced at the surface of the membrane by a reducing agent coming from the acceptor stream that AHQ permeation can occur. It was also shown that increasing surface coverage of the membrane through AQ particle size reduction could improve the rate of membrane permeation.

This has direct implications for pulping. The mechanism described by the model system was then tested against pulping data. It was shown that the addition of surfactants could increase the pulping efficiency of AQ. This is probably through better dispersion

of AQ particles to cover more chip surface area. Bulk reduction effects were also tested, and it was shown that bulk phase reducing agents decrease the efficacy of AQ in pulping. This led to the development of the mechanism for AQ diffusion in alkaline pulping.

This mechanism was put to the test by a preliminary round of pulping experiments, designed to test the three main parameters identified in the mechanism that affect AQ diffusion: rise time, initial AQ particle size, and the rate of the surface reaction. Though most of the results of this early experimental run are inconclusive, nonetheless it shows that this mechanism holds promise for improving the effectiveness of AQ in alkaline pulping.

CHAPTER 1

INTRODUCTION

The focus of the pulping industry is once again shifting. Where once environmental factors and cost-cutting were the driving factors for innovation and research, new opportunities are arising. Particular among these is the use of biomass for other applications such as fuels.

As more and more trees begin to be used as the basis for fuels, the industry will find itself with less and less virgin fiber supply with which to work. Thus yield-enhancing chemical additives such as anthraquinone (AQ) should see increased use. Anthraquinone is particularly interesting because of its dual role as enhancer of both delignification and yield. Improving the carbohydrate yield while maximizing delignification can lead to clean sources of simple sugars. These can then be used in generating ethanol through fermentation. Especially, saving and isolating the non-structural components of wood (i.e. hemicelluloses) could lead to a new income stream for pulp mills while maintaining most of the pulp quality. This could also remove some of the burden that ethanol production currently places on the world's food supplies.

Therefore it is beneficial to fully understand the mechanism by which AQ works in pulping in order to maximize the activity of the additive. Ever since AQ was first introduced to the paper industry in 1977 [1], researchers have been trying to discover the reasons that this additive works so well in accelerating delignification and preserving yield. Studies ranging from forays into elucidating the chemical mechanism of the AQ-lignin reaction to exploration of the chemical reaction kinetics have led to the current

understanding of the pulping additive. Still, these do not create a full understanding of the action of AQ.

One item which still eludes understanding is the physical mechanism for AQ transport in wood. Because of its insolubility in aqueous solution, AQ has a difficult path to reach the carbohydrates inside the wood chips. This present work seeks to improve the understanding of the action of AQ with respect to its mass transfer during pulping.

CHAPTER 2

LITERATURE REVIEW

Mass Transfer and Diffusion

Diffusion is the process by which matter moves in a system as a result of random molecular interactions. Adolph Fick was the first to postulate a theory of the movement of mass by diffusion [2]. He based this idea on analogy to Fourier's law of heat conduction [3]. Originally, his idea could not account for the differences in materials and diffusing species. Today, we have a much better understanding of the process of diffusion.

Principles of Diffusion

The one-dimensional diffusional flux (J) of a species A in another species B is given by Fick's first law:

$$J_x = -D\frac{\partial C}{\partial x} \tag{2.1}$$

where D is the diffusion coefficient and $\partial C/\partial x$ is the concentration gradient in the x-direction [4]. From the conservation of mass, the rate of the concentration change must be equal to the rate of change of the flux. Thus,

$$\frac{\partial C}{\partial t} = \frac{\partial J_x}{\partial x} \tag{2.2}$$

Combining Equations 2.1 and 2.2 yields the differential equation for diffusion known as Fick's second law:

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2} \tag{2.3}$$

These equations (2.1 and 2.3) form the basis for understanding mass transfer in various systems and geometries [4].

Diffusion in Membranes

A membrane can be defined as a permeable plane sheet whose dimensions are such that the diffusion is effectively one dimensional; i.e. one dimension is considerably smaller than the other two, so that diffusion through the larger edges is negligible. This is the definition that will be used in the following analysis.

Equilibrium

At steady state the diffusion into the membrane has reached equilibrium, and the concentration at all points of the membrane are constant. Therefore,

$$\frac{d^2C}{dx^2} = 0 \tag{2.4}$$

as long as the diffusion coefficient is constant. Integrating this with respect to x yields

$$\frac{dC}{dx} = a \tag{2.5}$$

where a is a constant. For a membrane of thickness l, further integration yields

$$\frac{C - C_1}{C_2 - C_1} = \frac{x}{l} \tag{2.6}$$

where C_1 is the concentration at x=0 and C_2 is the concentration at x=l. This enables determination of the concentration at any point in the membrane assuming a linear concentration profile [4].

It also enables experimental determination of the diffusion coefficient. Since

$$J_x = -D\frac{dC}{dx} = -D\frac{C_2 - C_1}{l} \tag{2.7}$$

measuring the flux across the membrane for a known concentration gradient will yield the diffusion coefficient.

Non-steady state

Transient data can also be used to determine the diffusion coefficient. In the case of transient membrane permeation, one face of the membrane (x=0) is kept at a constant C_1 and the other face (x=l) is kept at C_2. If the membrane has an initial uniform concentration C_0, there is a finite time before the equilibrium of the previous section occurs. During this time, the concentration changes according to

$$C = C_1 + (C_2 - C_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{C_2\cos n\pi - C_1}{n}\sin\frac{n\pi x}{l}\exp\left(-Dn^2\pi^2 t/l^2\right)$$

$$+\frac{4C_0}{\pi}\sum_{m=1}^{\infty}\frac{1}{2m+1}\sin\frac{(2m+1)\pi x}{l}\exp\left\{-D(2m+1)^2\pi^2 t/l^2\right\} \qquad (2.8)$$

As $t \to \infty$, the exponential terms drop out, and the concentration becomes linear according to Equation 2.6.

According to Fick's first law, then, the flux from the exiting surface of the membrane (x=l) is proportional to the rate of change of concentration at that surface with respect to x. Integrating this at x=l with respect to time gives the cumulative mass of a diffusing substance exiting a membrane (Q_t)

$$Q_t = D(C_1 - C_2)\frac{t}{l} + \frac{2l}{\pi^2}\sum_{n=1}^{\infty}\frac{C_1\cos(n\pi) - C_2}{n^2}\left\{1 - \exp-\left(Dn^2\pi^2 t/l^2\right)\right\}$$

$$+\frac{4C_0 l}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\left\{1 - \exp\left(-D(2m+1)^2\pi^2 t/l^2\right)\right\} \qquad (2.9)$$

If both C_2 and C_0 are zero, a common experimental setup in membrane experiments, this equation reduces to

$$Q_t = lC_1\left\{\frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left[\frac{-Dn^2\pi^2 t}{l}\right]\right\} \tag{2.10}$$

As time lengthens such that $t \to \infty$, this equation approaches the line

$$Q_t = \frac{DC_1}{l}\left(t - \frac{l^2}{6D}\right) \tag{2.11}$$

The t-intercept of this line (θ_D) is known as the time lag of the experiment, and it is given by

$$\theta_D = \frac{l^2}{6D} \tag{2.12}$$

Thus, the diffusion coefficient can be determined by measuring the time lag of a transient membrane experiment as it approaches steady state [4].

Diffusion with Chemical Reaction

In some cases a diffusing species can be reactive with the substance through which it is diffusing. This will have a direct impact on the rate of diffusion as some of the diffusing species is effectively immobilized in the system. However, when the reaction is reversible, the diffusion behavior depends on the relative rates of diffusion and chemical reaction.

If the rate of reaction is very rapid, then the immobilized component is always in equilibrium with the diffusing species, and the process is diffusion controlled. If, however, the diffusion is significantly faster than the reaction, the concentrations of the diffusing species and the immobilized component are uniform throughout the medium. In this case the behavior is determined by the reaction rate.

When the relative rates are equivalent, the diffusion is governed by the equation

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t} \tag{2.13}$$

where C and S are the free species and the immobilized species, respectively. The rate of formation of the immobilized species is given by

$$\frac{\partial S}{\partial t} = k_f C - k_b S \tag{2.14}$$

where k_f and k_b are the forward and backward reaction rates, respectively. The rate of formation of the immobilized species is proportional to the concentration of the diffusing species, and the rate of dissolution is proportional to the concentration of the immobilized species [4]. Thus both the rate of diffusion and the rate of reaction are taken into account for this reaction system.

External Mass Transfer Resistances

So far, this review has focused on diffusion inside a porous body. However, when there is more than one phase present, boundary layers form. The mass transfer across these layers may or may not be negligible compared with the internal mass transfer. One way to determine this is with the mass transfer Biot number (or Damköhler number), Bi_m:

$$Bi_m = \frac{h_m \delta}{D_{AB}} \tag{2.15}$$

where h_m is the film mass transfer coefficient, δ is the boundary layer thickness, and D_{AB} is the molar diffusivity. This is the ratio of the internal and external mass transfer resistances (or the ratio of the external mass transfer rate to the internal mass transfer rate [5]). If this number is large ($Bi_m > 1$), external mass transfer resistance can be assumed to be negligible.

Structure of Wood

Wood has been used by man for ages as a source of fuel and structural materials. The use of wood as a fiber source for papermaking is relatively recent, as most early papers were made from rags. It is important to note the structure of wood here, so that understanding the mass transfer processes through it is possible.

Chemical Composition

Wood is mostly made up of carbon, hydrogen, and oxygen arranged in three main polymers: cellulose, hemicellulose and lignin. It also contains a portion of inorganic compounds. When wood burns, these inorganics make up the ash. Table 2.1 gives the elemental makeup of wood, and Table 2.2 gives some indication of the distribution of the organic polymers in wood.

Table 2.1: Elemental composition of wood [6].

Element	% dry weight
Carbon	49
Hydrogen	6
Oxygen	44
Nitrogen	>0.1
Ash	0.2-0.5

Table 2.2: Distribution of polymers in wood [6].

Type	Cellulose	Hemicellulose	Lignin
		% dry weight	
Hardwood	40-44	15-35	18-25
Softwood	40-44	20-32	25-35

Cellulose is the main component of wood, making up just under half of the total mass of the wood. It is a homopolymer of glucose attached via 1-4 ether linkages

arranged in a straight, unbranched chain. The degree of polymerization is around 10,000 [6]. Because of its structure, it can have both crystalline and amorphous regions. These crystalline regions are fairly impervious to chemical attack.

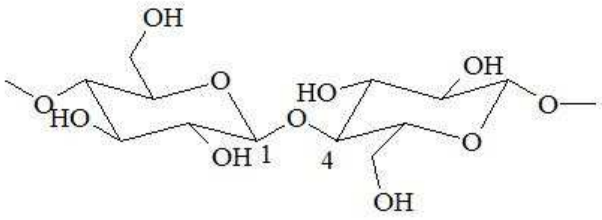

Figure 2.1: Cellobiose repeating unit for cellulose.

Cellulose is the most important wood component in papermaking. It provides the strength and bonding necessary to form a paper web. Most importantly, it is colorless, so it can make a very white sheet.

Each cellulose chain contains a reducing end unit. This is the last glucose unit on the chain. It is the only glucose unit free to decyclize – forming the aldehyde. This unit is most open to attack during pulping.

Hemicellulose is a polysaccharide made from different sugar units. In softwoods, the main hemicellulose component is glucomannan. In hardwoods, the main component is xylan. Hemicelluloses are relatively short chained (compared to cellulose) and often contain side chains. These are mostly used to give flexibility to fibers and to provide a link between lignin and cellulose units.

Lignin is the glue that holds all of this together. It is a highly cross-linked polymer made up of three different building blocks. These building blocks are important because they affect the behavior of the lignin during pulping. The first block, *p*-coumaryl alcohol, is not very prevalent in wood, but can be found in reaction wood and grasses.

Coniferyl alcohol is the main building block in softwoods, but is also present in hardwoods. In native lignin, bonded coniferyl alcohol units are referred to as guaiacyl units. Sinapyl alcohol is found only in hardwoods. In native lignin bonded sinapyl alcohol units are referred to as syringyl units. A greater number of units attached to the benzene ring decreases the irreversible condensation reactions that occur during pulping.

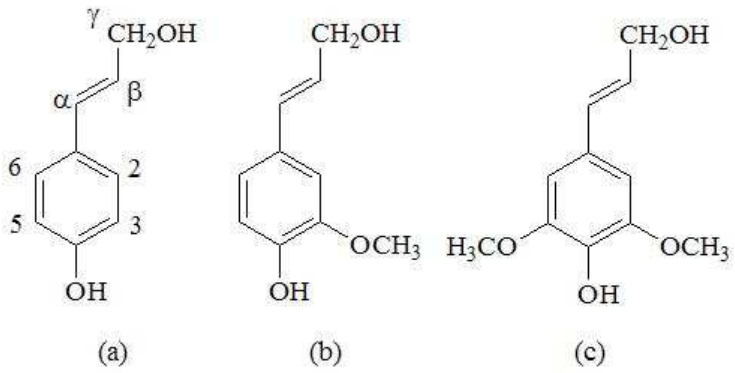

Figure 2.2: Building blocks for lignin: (a) *p*-coumaryl alcohol, (b) coniferyl alcohol, (c) sinapyl alcohol.

The side chains can also inhibit the formation of cross-linking bonds that cannot be removed during pulping. Figure 2.3 shows a partial structure of a lignin macromolecule for a softwood. There are several different links between building blocks. The easiest to remove are the ether linkages, while carbon-carbon bonds are impossible to break during cooking.

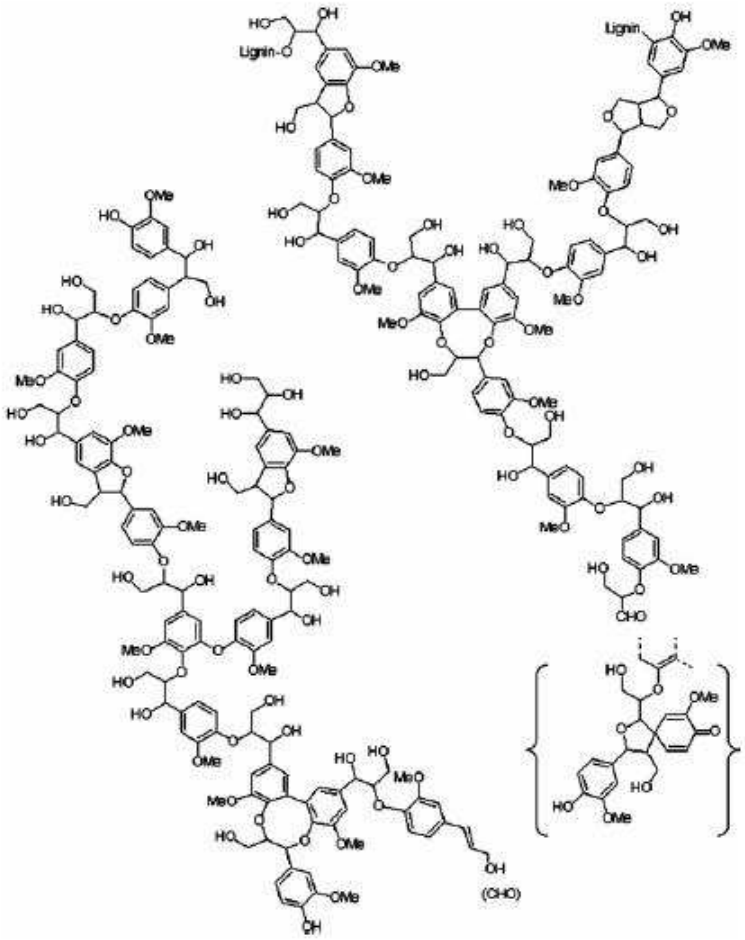

Figure 2.3: Schematic of softwood lignin macromolecule showing various types of cross-linking between alcohol units [7].

Macroscopic Structure

Wood has three main faces, as shown in Figure 2.4. These are the transverse surface, which is the surface seen on a stump, the radial surface, and the tangential surface. These terms will help orient the structures to be discussed.

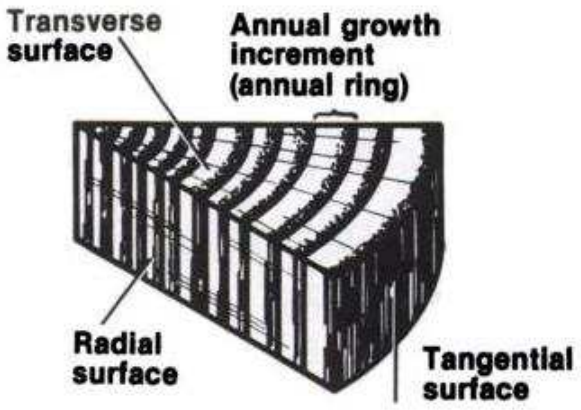

Figure 2.4: Cross section of wood showing different surfaces [6].

Young trees are primarily made of sapwood, which is active in the transport of water and chemicals up the trunk. Older trees also contain heartwood, which is mainly used for storage of chemical resins. Both sapwood and heartwood are divided into annual rings, which are most easily viewed from the transverse face. These rings are the result of the different density cells the tree produces during the growing season. Earlywood is formed in the spring, at the time when nutrients are plentiful and growth is rapid. These cells are characteristically lighter and less dense than latewood. Latewood is darker and more dense, forming later in the year. The transverse view shown in Figure 2.5 shows the latewood and earlywood for a conifer.

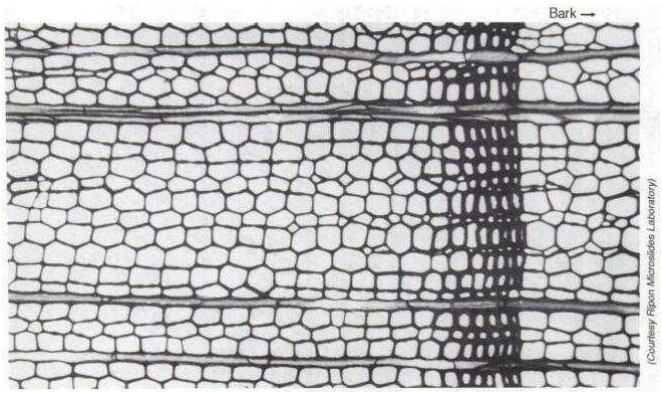

Figure 2.5: Transverse view of redwood showing the difference between earlywood (more open structure) and latewood (denser cells) [6].

Microscopic Structure

The most important aspects of the microscopic structure of wood for pulping are the cell wall and the inter-cell pits. These are the paths through which pulping chemicals reach the inside of the wood chips.

The cell wall is divided into two main sections: the primary wall and the secondary wall. The primary wall is highly lignified with cellulose in a random pattern. Most of this cellulose is amorphous.

The secondary wall is further subdivided into smaller layers, depending on the orientation of the cellulose fibrils. The S1 and S3 layers have high fibril angles relative to the cell axis. The S2 layer fibrils are almost vertical to the cell axis. The S2 layer provides the cell wall with its tensile strength, while the other two layers keep these from falling apart under longitudinal strain. Figures 2.6 and 2.7 show the structure and chemical makeup of the cell wall layers, respectively.

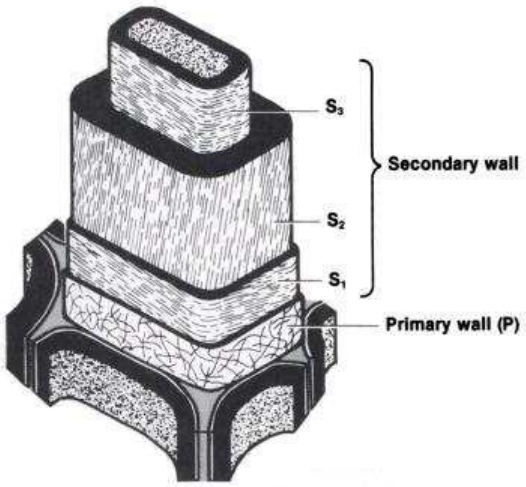

Figure 2.6: Schematic of the cell wall showing the primary and secondary walls, surrounded by inter-fiber lignin [6].

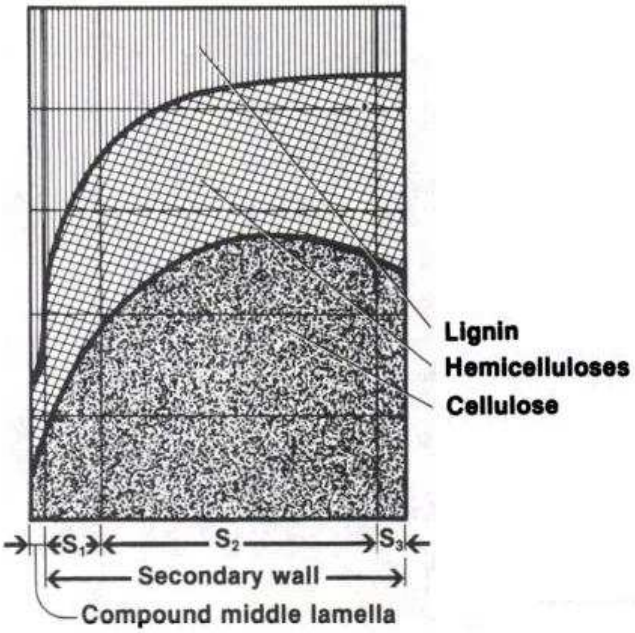

Figure 2.7: Distribution of chemicals making up the cell wall [8].

Pits in the cell wall allow water and other chemicals to move between different cells. These are usually located on the tapered ends of cells, but they may also be found

where the cell borders a ray (longitudinally oriented short cells that carry nutrients from the center of the tree to the outer surface).

Pits come in different forms. The most common in wood is the bordered pit pair, but simple pits and half-bordered pit pairs are also present. These are shown schematically in Figure 2.8.

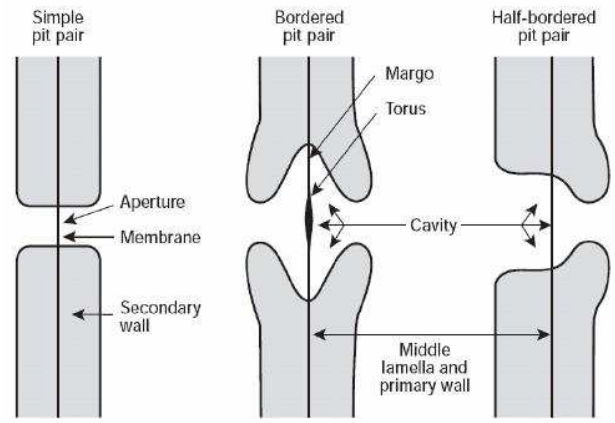

Figure 2.8: Schematic of different types of pits present in wood cells [9].

These pits can become occluded, especially in dry wood. When wood dries, the margo in a bordered pit pair will often fall to one side of the pit pair. The torus then forms a sort of cork to seal off the pit. The pit cannot be reopened once this has occurred.

Wood Chips

Wood logs must first be broken up into chips for chemical pulping. This enhances pulping by increasing the surface area of wood in contact with the chemicals and creating shorter diffusion pathways. Chips are carefully screened according to size, though the important dimension for pulping is the chip thickness.

Because the chip's thickness is its smallest dimension, this is the most important for diffusion. Chips are generally 10-30mm in length and width, but only 3-6mm in thickness [10]. This enables viewing diffusion as mostly one dimensional. Very thin chips can experience overpulping, leading to a decrease in yield. Over-thick chips may be too thick to allow pulping chemicals to reach the center, leading to charring of the wood at the high temperatures in the digester and increased rejects in pulp screening.

Alkaline Pulping

The main purpose of chemical pulping is to remove lignin from the wood and separate the remaining carbohydrate structures into individual fibers. This is mostly done in alkaline processes at high temperatures, though both acidic and neutral processes are used as well. Organic solvents may also be used to delignify wood, either alone or in conjunction with inorganic acid or alkaline solvents [11].

The main alkaline process is known as the kraft process. It has several advantages over other processes, including low cost of chemicals, ease of chemical recovery, etc. However, it has the drawback of using sulfurous compounds, which, when reduced, create a very negative odor. It is this odor, among other things, that has added to poor environmental credentials of the paper industry.

Penetration

The first step in moving chemicals into the wood chips is penetration. This is the flow by capillary pressure and external pressure of the liquor into the lumen (open cavities in the center of the cell). Penetration is very important in pulping, and has a great impact on the quality of the resulting pulp [12-14].

Chips are first presteamed to remove air from the lumen and to provide heat to the chips. Cooler white liquor is then introduced. This causes the steam in the lumen to condense, pulling white liquor into the chip. This occurs mostly along the longitudinal direction of the chip, as the liquor passes from cell to cell through the pits [15].

The total pressure gradient acting on the chip (P_T) is given by the sum of the external pressure (P_E) and the capillary pressure (P_C):

$$P_T = P_E + P_C \tag{2.16}$$

The capillary pressure is given by the Young-Laplace equation:

$$P_C = \frac{2\gamma \cos\theta}{r} \tag{2.17}$$

where γ is the surface tension of the liquor, θ is the contact angle between the liquor and the chip surface, and r is the radius of the capillary in the chip. The capillary pressure has an opposing pressure due to the flow of liquid through the capillary:

$$P_F = \frac{8\eta v l}{r^2} \tag{2.18}$$

where η is the viscosity of the fluid, v is the penetration velocity, and l is the length of penetration into the chip. Therefore, the white liquor will penetrate into the chip a distance l until the opposing pressure is equal to the forcing pressures:

$$P_F = P_E + P_C \tag{2.19}$$

Combining Equations 2.16-2.18 gives an expression for the distance into the chip that the liquor will travel:

$$l = \frac{r^2}{8\eta v}\left(P_E + \frac{2\gamma \cos\theta}{r}\right) \tag{2.20}$$

Thus, penetration is highly dependent on the radius of the capillaries in the wood. This indicates that wood with smaller cell lumens will be more difficult to penetrate. This has implications in the uniformity of pulping, as lumen diameter differs between wood species, and within the wood itself, as heartwood has smaller lumens than sapwood and latewood has smaller lumens than earlywood.

As penetration progresses, any entrained air will be compressed by the ingressing white liquor. In order to achieve full penetration of the chip, this air needs to be removed. The only way to do this is for the air to dissolve into the liquor and move out via diffusion. This is called secondary penetration. Here, the thickness dimension becomes more important, since that is the shortest diffusion length.

Diffusion

Wood is generally agreed upon to be an anisotropic material. However, in the presence of strong alkali, fibers in the wood swell, creating a material that has similar diffusion characteristics in all directions [16, 17]. The result of this is that the ability of chemicals to diffuse to the center of the chip depends most greatly on the chip thickness because it is the smallest dimension of the chip.

The thickness of the chip has been shown to be a major factor influencing the homogeneity and the rate of the pulping reaction [17-20]. Figure 2.9 illustrates the effect of chip thickness on screen rejects. The thicker chips have much higher reject rates than the thinner ones [20]. This is to be expected, as the chemicals in cooking have a longer distance to diffuse to the center. Therefore, incomplete and/or inhomogeneous pulping occurs at the center of the chip.

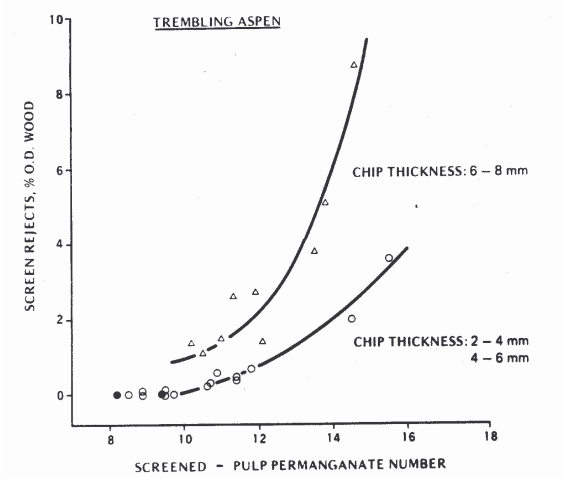

Figure 2.9: Diagram of the effect of chip thickness on the amount of rejects [20].

Poor impregnation is the result of improper control over the initial pulping conditions (i.e. time, temperature, and chemical concentration) [13]. If the temperature of the cook is raised too fast, then the delignification rate will outpace the rate of chemical diffusion. In this case, the center of the chip will become burned in sulfite pulping or severely degraded in kraft and soda pulping because of heating in the absence of pulping chemicals [14]. The chemicals cannot reach the center of the chip before being used up in delignification reactions. In order to avoid diffusion limitations, chips should not be too thick, or the temperature should not be too high before achieving good impregnation of the chips.

Lignin Reactions

Lignin reactions in alkaline pulping operations can be divided into three distinct phases: initial delignification, bulk delignification, and residual delignification. These phases are shown graphically in Figure 2.10.

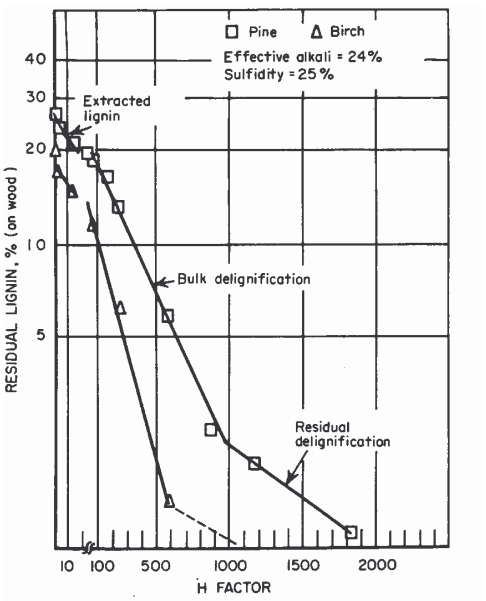

Figure 2.10: Residual lignin content of pine and birch wood during cooking [10].

In the initial phase, only a very small amount of lignin is removed. Only the most easily removed lignin pieces are cleaved during this phase. This accounts for the low activation energy of about 50 kJ/mol for initial delignification [21].

The lignin units removed during the initial delignification phase are those that contain free phenolic hydrogen atoms. During initial delignification, these are removed by hydroxide ions in the liquor. This leads to the formation of quinone methides, breaking any α-ether bonds. The α carbon now has a slight positive charge, and is a good target for nucleophilic attack from a hydroxide ion (or hydrosulfide ion in kraft pulping). A hydroxide ion can remove the now acidic hydrogen atom from the new alcohol unit. The resulting negatively charged oxygen (or sulfur) atom can then form an epoxide (episulfide) between the α and β carbons, breaking the β-aryl ether bonds. One reason kraft pulping is much faster than soda pulping is because episulfides are much

more stable than epoxides under these conditions. This is shown schematically in Figure 2.11.

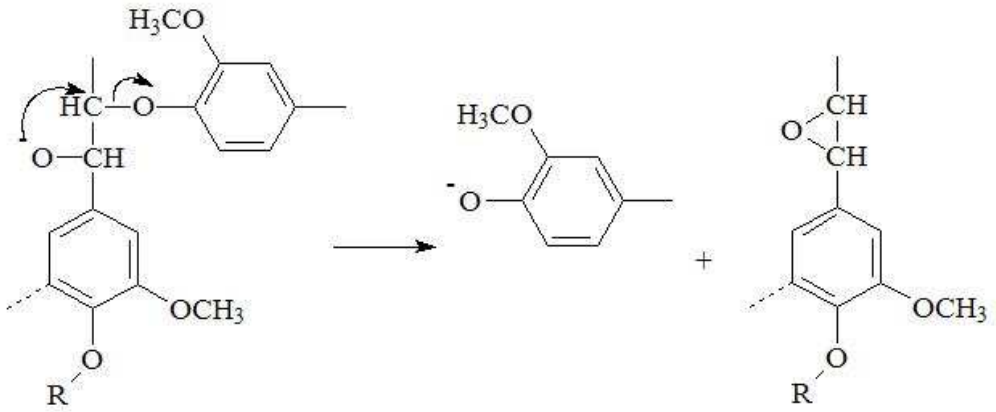

Figure 2.11: Schematic of delignification reaction [22]. R=H in initial phase.

Initial delignification can only remove one syringyl or guaiacyl unit at a time. During bulk delignification, small bundles of lignin units are removed. These must still be small enough to be soluble in the pulping liquor. Because of this, most of the lignin is removed during this phase. Though the activation energy for bulk delignification is considerably higher than that of initial delignification (130-150 kJ/mol [21]), this phase of the cook removes the lignin more rapidly because of its higher temperature.

Bulk delignification does not require the formation of a quinone methide to free up the α carbon for nucleophilic attack. If there is already a hydroxyl unit present, epoxide formation can occur. This means that there can be both α-β epoxides and β-γ epoxides during bulk delignification. These are the main reactions during delignification.

During the bulk phase, there are some competing reactions that lead to lignin condensation. These are usually the result of the formation of carbon-carbon bonds that

cannot be broken by the pulping chemistry. This often leads to darker pulps that are harder to bleach.

Because the conditions of pulping involve changes in temperature over time, it is difficult to determine the extent of pulping from the temperature profile alone. Therefore, a single unit based on the rate of the lignin reactions was developed that encompasses both time and temperature. This system is based around the rate of reaction relative to the rate at 100°C. When using a value for the activation energy of 134 kJ/mol (32.0 kcal/mol), the relative reaction rate is given by the empirical expression:

$$r = \exp\left(43.2 - \frac{16{,}113}{T}\right) \tag{2.21}$$

where r is the relative rate of reaction and T is the temperature (in Kelvins) at time t. The rate of reaction doubles for each 8-10°C increase in temperature. The time integral of the relative rate is called the H factor [23]:

$$H = \int_0^t \exp\left(43.2 - \frac{16{,}113}{T}\right) dt \tag{2.22}$$

If the concentrations of the reacting chemicals vary reproducibly, the extent of delignification can be predicted by the H factor [21]. This allows the pulp mill to have a simpler recipe, because only one factor is needed instead of two.

The H factor was developed before the absolute kinetics of alkaline pulping were known. The purpose was to unify time and temperature into one factor to give a simpler recipe in pulping, and to predict the changes that would be needed in cooking time or temperature due to fluctuations in the cooking cycle. In his development of the H factor, Vroom assumed an Arrhenius equation could adequately describe the temperature dependence of the absolute delignification rate. This way, a change in temperature would

increase the rate by a given factor irrespective of the absolute rate at those temperatures. Arbitrarily setting the relative rate of reaction at unity for a temperature of 100^{o}C, and utilizing the reaction rate data from an earlier source [24], Vroom developed the above expression [23].

Vroom then tested his theory against pulping data and found that lignin contents of a series of pulps collapsed to a single trend line when plotted against his H factor. This held for kraft pulping, but not for soda pulping. This is probably due to the higher activation energy for soda pulping. Nonetheless, with adjustments to the constants in the above Equation 2.22, the H factor theory holds for soda pulping as well [23]. Because of its utility and simplicity, the H factor is still widely used, even though the absolute kinetics for the delignification reaction are known.

The utility of the H factor lies in this ability to predict the outcome of pulping. If a certain pulp Kappa number is desired, then changes to the pulping temperature can be adjusted with increased or decreased time of pulping. This leads to a very good control over the lignin content of the pulp leaving the digester, even with large perturbations in pulping conditions. This is especially important for bleachable grades, where the amount of lignin left in the pulp determines the amount of bleach needed downstream. This then has direct impacts on operating costs.

Carbohydrate Reactions

There are two main reactions by which the carbohydrates in the fibers are degraded. These are endwise peeling and chain cleavage. The former involves the cleavage of reducing end groups, while the latter includes scission of the chain at a random point, forming two shorter chains and a new reducing end group.

In endwise peeling, the reducing end group is attacked by hydroxide at C_2 while it is in its non-cyclic aldehyde form. This converts the aldehyde end unit into a 1,2-enediol form. This can then react with more hydroxide to form the corresponding ketose. The ketose can further react to form a 2,3-enediol. Removal of the C_2 hydroxy proton can then lead to the breaking of the C_4 ether bond with the neighboring unit. The cleaved unit then undergoes benzylic acid rearrangement (BAR) to form an isosaccharinic acid [21]. The cleaved ether bond allows the new end group to undergo the same process. Thus the end groups of the carbohydrates can be removed one at a time.

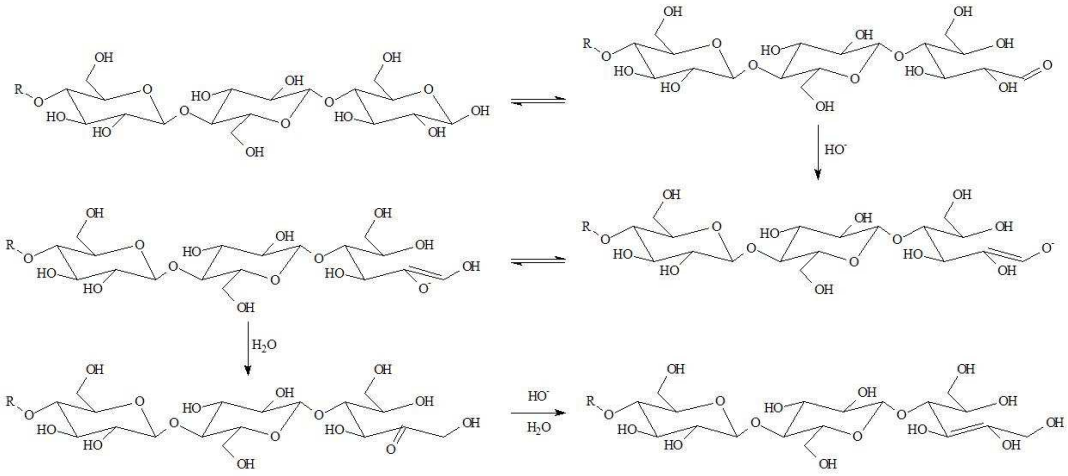

Figure 2.12: Formation of 2,3-enediol in reducing end group of cellulose.

Running counter to this is the so-called stopping reaction, or end group stabilization. In this case, cleavage of the hydroxyl unit at C_3 occurs before the conversion to the 2,3-enediol form is formed. Then through enolization and benzylic acid rearrangement, the still-attached end unit is converted to a metasaccharinic acid group. This metasaccharinic acid cannot undergo further reactions to form a 2,3-enediol, so cleavage of the ether bond at C_4 is not possible.

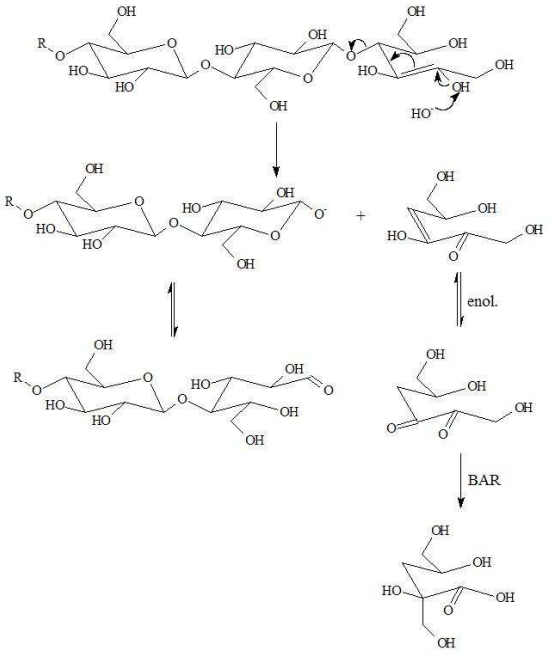

Figure 2.13: Endwise peeling with formation of new reducing end group and glucoisosaccharinic acid.

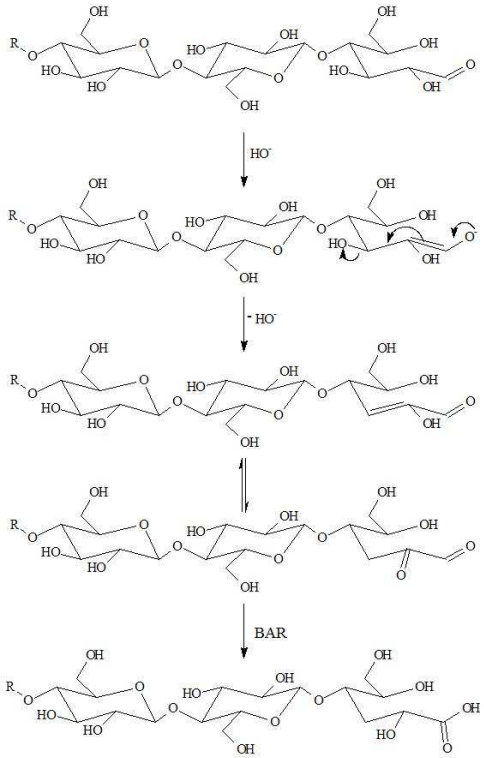

Figure 2.14: Stopping reaction forms a metasaccharinic acid group in the reducing end group, preventing further degradation.

Because the hydroxyl group is a poorer leaving group than the glucosyl group, the stopping reaction is much slower than the peeling reaction. There are approximately 60-65 end units peeled per end unit stabilized [25]. This is acceptable for cellulose with its degree of polymerization of 10,000 to 15,000. However, this constitutes a significant loss of the hemicellulose faction that usually has a degree of polymerization of about 100.

Also aiding cellulose is its partial crystallinity. The crystalline regions are not accessible by hydroxyl ions, so they cannot begin the process of degradation at the end groups, even if there has been no stopping reaction.

Chain cleavage involves the internal nucleophilic substitution of a conjugate base at the C_2 position. When the C_2 hydroxyl group is deprotonated in caustic, the oxy anion can form an epoxide with C_1, cleaving the C_1-O bond. The new epoxide end group then reacts with hydroxyl anions to form a new reducing sugar. This involves a large amount of energy, because ring flipping is required for epoxide formation. This reduces the distance between C_1 and C_4, causing the entire polysaccharide chain to contract slightly. Thus this cannot happen in the crystalline regions.

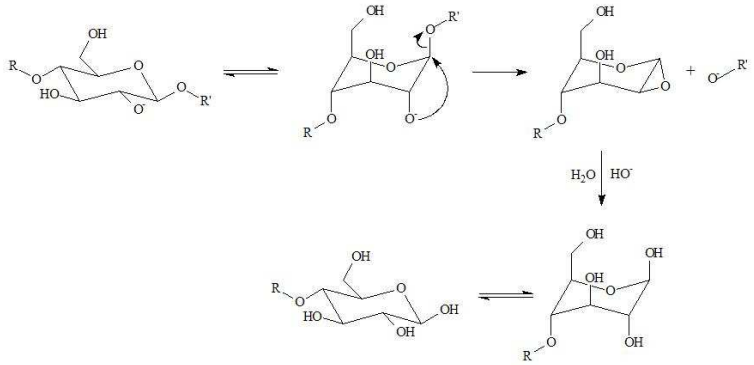

Figure 2.15: Chain cleavage reaction for cellulose results in the formation of a new reducing end group and a new non-reducing end.

Anthraquinone

Anthraquinone (AQ) is a three-ringed aromatic organic compound made up of carbon, hydrogen, and oxygen. Its structure is shown in Figure 2.16. It exists usually as a yellowish to light tan powder. AQ is planar and usually forms monoclinic crystals.

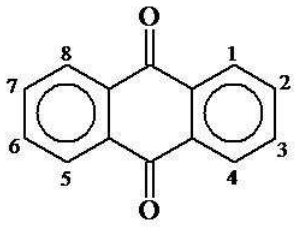

Figure 2.16: Anthraquinone with binding sites labeled.

Manufacture

There are several methods for manufacturing anthraquinone. The most obvious is the direct oxidation of anthracene to AQ [26, 27]. This, the dominant method for generating AQ, is usually conducted in the vapor phase at high temperature over a complex catalyst [27]. A second pathway is through Diels-Alder reaction [28], which is useful for generating substituted anthraquinones. A third pathway is the reverse of this, the Rickert-Alder reaction [29], though this method is not used to a great extent industrially. A fourth method is through Friedl-Crafts substitution of benzene and phthalic anhydride (a byproduct of AQ generation from anthracene [27]), with subsequent cyclization through dehydration [30].

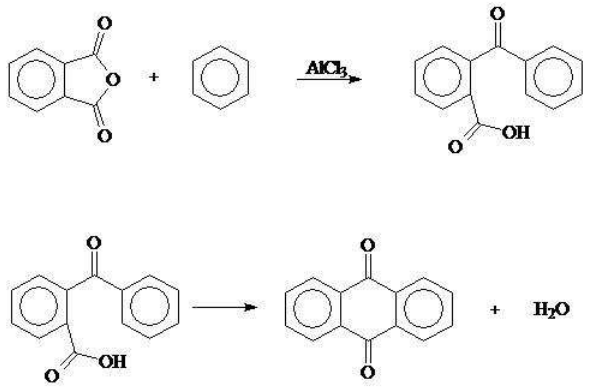

Figure 2.17: Reaction mechanism for Friedl-Crafts substitution/dehydration for AQ manufacture.

Pulping chemistry

Ever since Holton [1] first showed the benefits of pulping with AQ, researchers have been trying to understand the chemistry that gives AQ its excellent ability to catalyze alkaline pulping [31]. AQ has been generally shown to operate in a redox cycle in the duration of the chemical cook [31-34]. Carbohydrates dissolved in the pulping liquor and the reducing end groups of carbohydrates (which are oxidized to form aldonic acid groups) reduce the AQ to anthrahydroquinone ($AHQ^{\bullet}$ or $AHQ^{=}$). The oxidation states of AQ are shown in Figure 2.18. It then reduces lignin quinone methides to cleave a β-aryl ether bond in the lignin. The cycle is confirmed by an experiment conducted by Fullerton [35]. He found that oxygen in the air decreases the effectiveness of AQ pulping by oxidizing the AHQ in the system back to AQ. In a system where the digester was flushed with argon prior to pulping, Fullerton found that delignification was improved over those cooks where air was not excluded.

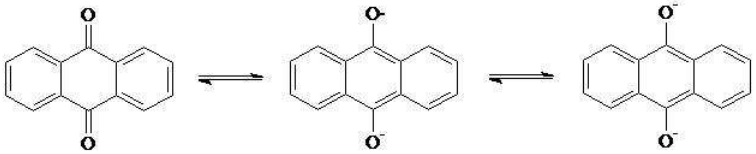

Figure 2.18: Oxidation states of anthraquinone. From left to right: anthraquinone (AQ), anthrahydroquinone radical anion ($AQ^{\cdot-}$), and anthrahydroquinone (AHQ^{2-}).

Originally, the mechanism of AQ in alkaline pulping was thought to be similar to hydrosulfide ions in kraft pulping. The thought was that an AHQ^{2-} molecule would bond to a lignin quinone methide, forming an adduct. This adduct would then undergo an elimination reaction that regenerated AQ and caused the β-aryl ether linkage in the lignin molecule to cleave. Although this may be a feasible mechanism, research has shown that this may not be the correct mechanism [33].

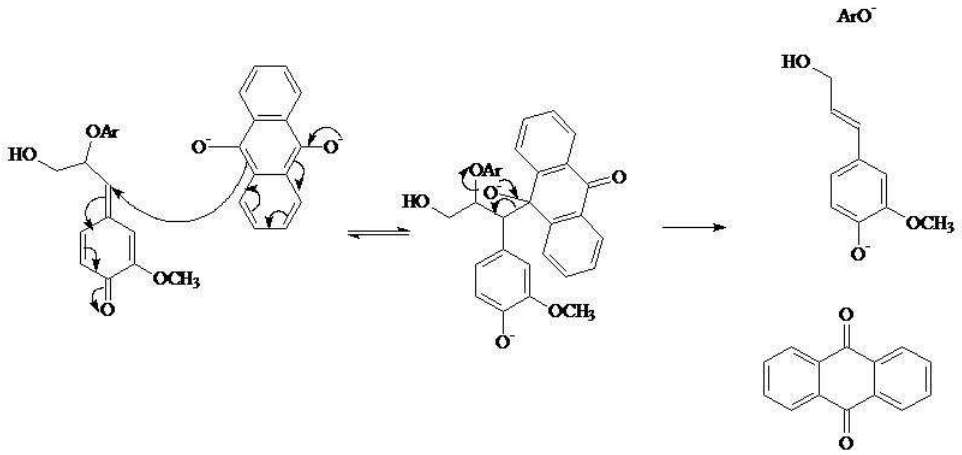

Figure 2.19: Adduct mechanism for AQ-aided delignification.

If AQ required the formation of an adduct during pulping, the effectiveness of AQ derivatives would be affected by molecular size. A bulkier compound would have a more difficult time forming an adduct with a quinone methide. In order to test this, a

sterically hindered AQ derivative was tested in pulping, and found to be nearly as effective as AQ [36]. Later experiments showed that the "bulkiness" of an AQ derivative has no effect on the effectiveness of the additive in pulping [37].

There are other data supporting a non-adduct mechanism. Researchers have shown a different mechanism for the action of AQ in pulping through electrochemical studies [33, 34] and studies with radical scavengers [33]. These studies indicate that a likely mechanism for AQ in pulping is single electron transfer (SET).

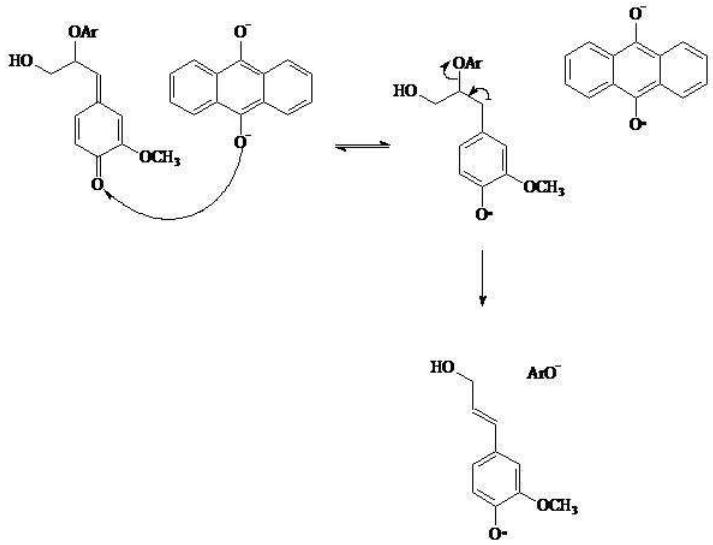

Figure 2.20: SET mechanism for AQ-aided delignification.

The SET mechanism involves the transfer of a single electron from AHQ^{2-} to the α-carbon of a lignin quinone methide. In order to relieve the added charge, the α-carbon forms a second bond with the β-carbon, causing the β-aryl ether bond to cleave. The $AHQ^{\cdot-}$ radical anion thus formed can gain an electron from a carbohydrate molecule such as the reducing end group of a cellulose chain to regenerate the AHQ^{2-} dianion [33].

It is also possible for the radical anion to transfer a second electron to form solid AQ. This could be an important step in the diffusion of AQ species into the chip. Both AHQ^- and AHQ^{2-} are completely soluble in the pulping liquor, whereas AQ is not. The formation of AQ could hinder the progress of AQ species deeper into the chip, and alter the pulping results.

Anthraquinone Mass Transfer in Alkaline Pulping

Anthraquinone is an interesting study for diffusion because it requires reaction to become mobile. In fact, it would be impossible to study "AQ diffusion" because as an insoluble species, AQ cannot diffuse. However, when it is reduced, the AHQ becomes soluble in pulping liquor, allowing for diffusion. However, there is also oxidation during the cook, and AQ deposits out of solution. This is a classic case study for diffusion with reversible chemical reaction discussed above.

In pulping, one must not only account for the reaction, but also any sorption of the diffusing species on chip surfaces. Therefore, a modified version of Fick's second law, including both reaction and sorption terms is used:

$$\frac{\partial\left(\varepsilon_i C + \rho_c X\right)}{\partial t} = ECCSA \times D\frac{\partial^2 C}{\partial w^2} - \frac{\partial S}{\partial t} \tag{2.23}$$

where ε_i is the void fraction inside the chip (m^3 voids/m^3 wood), ρ_c is the basic density of chip (g wood/m^3 wood), X is the chemical consumed by sorption (g adsorbed/ g wood), ECCSA is the effective capillary cross sectional area (m^2 open/m^2 surface), and w is the thickness dimension of chip (m). This is not derived directly from Fick's second law, but instead from the mass balance inside the chip, in the same way as Fick's second law is derived.

For a catalytic pulping additive such as anthraquinone (AQ) and its derivatives, one must account for the reaction which changes the form of the additive to the reduced or oxidized form. This is easily done for soluble derivative of AQ such as anthraquinone-2-sulfonic acid (AQ-S):

$$\frac{\partial\left(\varepsilon_i C_{AQ-S} + \rho_c X_{AQ-S}\right)}{\partial t} = ECCSA \times D_{AQ-S} \frac{\partial^2 C_{AQ-S}}{\partial w^2} - r_{CS} + r_{PS} \tag{2.24}$$

where r_{CS} and r_{PS} are the rate of consumption of AQ-S and the rate of production of AQ-S from AHQ-S (reduced from of AQ-S), respectively.

This must be paired up with the diffusion of the reduced form of AQ-S because of the fast reaction:

$$\frac{\partial\left(\varepsilon_i C_{AHQ-S} + \rho_c X_{AHQ-S}\right)}{\partial t} = ECCSA \times D_{AHQ-S} \frac{\partial^2 C_{AHQ-S}}{\partial w^2} - r_{CHS} + r_{PHS} \tag{2.25}$$

where r_{CHS} and r_{PHS} are the rate of consumption of AHQ-S and the rate of production of AHQ-S from AQ-S, respectively.

If there are no side reactions, then

$$r_{CS} = r_{PHS} \tag{2.26}$$

and

$$r_{PS} = k_{CHS} \tag{2.27}$$

One can then add equations (2.24) and (2.25) to obtain the overall diffusion of AQ-S and AHQ-S in chips:

$$\frac{\partial\left[\varepsilon_i\left(C_{AQ-S} + C_{AHQ-S}\right) + \rho_c\left(X_{AQ-S} + X_{AHQ-S}\right)\right]}{\partial t}$$

$$= ECCSA \times \left(D_{AQ-S} \frac{\partial^2 C_{AQ-S}}{\partial w^2} + D_{AHQ-S} \frac{\partial^2 C_{AHQ-S}}{\partial w^2} \right) \tag{2.28}$$

This can be solved numerically to obtain a picture of the diffusion of AQ-S during impregnation of the chips, if the variables are known.

The model for AQ is different, however, because of its near insolubility in pulping liquors. One must take into account the fact that the only diffusing species is anthrahydroquinone (AHQ) and therefore, the concentration of AQ in the liquors is approximately zero. Thus, the equation for AHQ (2.29) is similar to those of AQ-S and AHQ-S, but the equation for AQ (2.30) is very different:

$$\text{AHQ: } \frac{\partial(\varepsilon_i C_{AHQ} + \rho_c X_{AHQ})}{\partial t} = ECCSA \times D_{AHQ} \frac{\partial^2 C_{AHQ}}{\partial w^2} - r_{CQ} + r_{PQ} \tag{2.29}$$

$$\text{AQ: } \rho_c \frac{\partial X_{AQ}}{\partial t} = -r_{CHQ} + r_{PHQ} \tag{2.30}$$

Here, the diffusion terms for AQ are removed, and the sorption is purely based on the rates of the forward and reverse reactions,

Assuming no side reactions again (i.e. $r_{CQ} = r_{PHQ}$ and $r_{PQ} = r_{CHQ}$), one can combine these equations to obtain an overall expression for the diffusion of A(H)Q in a wood chip:

$$\rho_c \frac{\partial(X_{AQ})}{\partial t} + \frac{\partial(\varepsilon_i C_{AHQ} + \rho_c X_{AHQ})}{\partial t} = ECCSA \times D_{AHQ} \frac{\partial^2 C_{AHQ}}{\partial w^2} \tag{2.31}$$

If X_{AQ} and X_{AHQ} are linear with respect to C_{AHQ}, the equation simplifies to Fick's law once again:

$$\frac{\partial C_{AHQ}}{\partial t} = D^*_{AHQ} \frac{\partial^2 C_{AHQ}}{\partial x^2} \tag{2.32}$$

where D^*_{AHQ} is given by

$$D^{*}_{AHQ} = \frac{ECCSA \times D_{AHQ}}{\varepsilon_i + \rho_c \left(\frac{\partial X_{AQ}}{\partial C_{AHQ}} + \frac{\partial X_{AHQ}}{\partial C_{AHQ}} \right)_T} \tag{2.33}$$

The $\partial X_{AHQ}/\partial C_{AHQ}$ term can be assumed to be negligible as it is much smaller than the $\partial X_{AQ}/\partial C_{AHQ}$ term, and Equation 2.33 reduces to

$$D^{*}_{AHQ} = \frac{ECCSA \times D_{AHQ}}{\varepsilon_i + \rho_c \left(\frac{\partial X_{AQ}}{\partial C_{AHQ}} \right)_T} \tag{2.34}$$

The D_{AHQ} term can be estimated using an empirical formula such as the Wilke-Chang equation:

$$D_{AB} = 1.173 \times 10^{-16} (\varphi M_B)^{1/2} \frac{T}{\mu_B V_A^{0.6}} \tag{2.35}$$

where φ is an "association parameter" of the solvent, M_B is the molecular weight of solvent (18 for water), T is the temperature in K, μ_B is the viscosity of solvent at temperature T in Pa s, and V_A is the molar volume of solute in m^3/ kg mol (0.2041 for AQ, 0.2546 for AQ-S, calculated from additive volumes reported by Le Bas [38]). Wilke and Chang [39] suggested that the association parameter, φ, is 2.6 for water, but a later work has suggested that a value of 2.26 gives a more accurate result [40].

For loblolly pine (*Pinus taeda* L.), Equation 2.34 can be rearranged, and some of the data filled in (ECCSA ≈ 0.2 at pH=14; $\varepsilon_i \approx 0.69$; $\rho_c \approx 0.464$ kg/L):

$$\left(\frac{\partial X_{AQ}}{\partial C_{AHQ}} \right)_T = 0.431 \frac{D_{AHQ}}{D^{*}_{AHQ}} - 1.49 \tag{2.34a}$$

Thus, the sorption properties of AQ can be determined from measuring the effective diffusivity of AHQ in wood.

The Wilke-Chang equation is an empirical refinement of the earlier Stokes-Einstein equation. The Stokes-Einstein equation was based on large spherical molecules diffusing in a solvent made of smaller spheres. The Wilke-Chang equation refined this to work for smaller, non-spherical molecules. Usually, the Wilke-Chang equation is useful for estimating the infinite dilution diffusion coefficients for molecules with molecular volumes below 0.500 m^3/kg mol [41]. AQ and its derivatives fall well within this range.

Wilke and Chang reported that their correlation estimated the diffusion coefficients with about 10% average error for 251 solute-solvent systems [39]. Reid et al. reported an average error of 7.6% for 14 aqueous systems [42]. In fact of the correlations Reid et al. examined for the 14 aqueous systems, the Wilke-Chang correlation had the lowest average error. Because of its ease of use and good accuracy for aqueous solutions, the Wilke-Chang equation is a good fit for estimating the diffusion coefficient for AHQ in water.

For concentrated solutions, one must take into account both the D_{AB} and the D_{BA}, or the diffusivities of both the solute and solvent in each other. The simplest way is to use the weighted mean of these:

$$D_{AB} = x_B D_{AB}^0 + x_A D_{BA}^0 \tag{2.36}$$

where x_B and x_A are the mole fractions of the solvent and solute, respectively, and the D_{XX}^0 terms are the infinite dilution diffusion coefficients obtained from one of the empirical formulae [43]. Another method is to use the geometric mean [44]

$$D_{AB} = \left(D_{AB}^0\right)^{x_B} \left(D_{BA}^0\right)^{x_A} \tag{2.37}$$

though this has some problems for mixtures containing an associating component. One common revision of these ideas is the introduction of a thermodynamic correction α, given by

$$\alpha = \left[\frac{d \ln a}{d \ln x} \right]_{T,P} \tag{2.38}$$

where a is the activity and x is the mole fraction. From the Gibbs-Duhem equation, this α will be the same for either the solvent or the solute [42]. This correction is multiplied to the D_{AB} obtained from the above equations to obtain a better match for the experimental data.

Another drawback to using these correlations is that they are usually only valid across a small temperature range. Geankoplis warns that the Wilke-Chang equation should be used with caution outside the temperature range of about 5-40°C [41]. However, Reid et al. indicate that the diffusion coefficient may have an Arrhenius relationship with temperature:

$$D_{AB}(or D_{AB}^{0}) = A \exp \frac{-B}{T} \tag{2.39}$$

where A and B are constants [42]. Another temperature relationship was also suggested:

$$\frac{D_{AB}^{0}(T_1)}{D_{AB}^{0}(T_2)} = \left(\frac{T_c - T_1}{T_c - T_2} \right)^{n} \tag{2.40}$$

where T_c is the critical temperature of the solvent, and n is related to the heat of vaporization of the solvent at the normal boiling point (n = 6 for water) [45]. It was reported that this gave an average error versus experimental data of about 9% [42].

CHAPTER 3

MASS TRANSFER IN AQ PULPING

Fleming, et al. demonstrated an interesting phenomenon in AQ pulping in their work in the late 1970s. Analysis of liquors and chip extracts showed that AQ concentrates in the chips to the point where the concentration there is higher than the concentration in the bulk liquor [34]. Later studies showed that AQ is less effective in displacement cooking than it is in conventional batch cooking [46, 47].

To provide a more satisfactory explanation for these observations, many of these earlier studies are here re-examined to include not only the effect of redox cycle and chemical mechanism, but also the effect of AQ mass transfer processes. This involves transfer between bulk liquid phase and chips and intra-chip transfer, as well as the solubility of different forms of AQ. By employing this approach, many earlier findings can be explained. More importantly, if these mechanistic interpretations can be confirmed by experimental study, they could provide guidance toward improving the efficiency of AQ in alkaline pulping. This portion of the work is a modified version of a previously published work [48].

Effect of AQ Dosage on Delignification Kinetics

Many studies around the world have been conducted in the last quarter-century on the effect of AQ on delignification kinetics. It is well established that the kinetics of kraft-AQ or soda-AQ delignification can be expressed as

$$-\frac{dL}{dt} = k_{AQ}^{*} AQ^{1/2}[OH^{-}]^{a}[HS^{-}]^{b} L^{c} \tag{3.1}$$

where *dL/dt* is the delignification rate, *L* is the lignin content in wood, k^*_{AQ} is the rate constant for the delignification reaction, $[OH^-]$ and $[HS^-]$ are the concentrations of hydroxide and hydrosulfide ions**,** *AQ* is the weight percentage of AQ charge based on oven-dry wood weight, and *a*, *b*, and *c* are constants [16, 49, 50]. For soda-AQ cooking, the $[HS^-]$ term can be ignored. It is important to note that this equation holds only over the limited range of concentrations studied here.

The form of Equation (3.1) is an ordinary power law kinetic equation. Of particular interest is the effect of AQ dosage. It affects the rate based on the amount of charge on wood weight, instead of its concentration in the liquid phase. The effect of AQ concentration on delignification kinetics is not apparent in many published reports. It is of importance to find out how the reaction kinetics are affected when the AQ concentration in the liquid phase is changed at a constant AQ dosage on wood. The following kinetic analysis using some published data is intended to illustrate this.

It was demonstrated that when delignification is divided into initial, bulk, and residual phases, each phase of the reaction is first-order on lignin [10, 16]. However, to develop a single, overall empirical rate equation, covering at least two phases, e.g., bulk and residual, it was found that the rate is better described by the second-order kinetics [16, 49, 50]:

$$-\frac{dL}{dt} = k_{AQ} AQ^{1/2} L^2 \tag{3.2}$$

where k_{AQ} is the reaction rate constant containing the effect of hydroxide and hydrosulfide ion concentrations.

Integrating this second-order rate, Equation (3.2) yields:

$$\frac{1}{L} - \frac{1}{L_W} = k_{AQ} A Q^{1/2} t \tag{3.3}$$

where L_W is the concentration of lignin in the original wood. The concentrations of lignin in the wood and pulps can be related to the Kappa numbers of the pulps with the following relationship:

$$L = \kappa \times 0.15 \times yield \tag{3.4}$$

for softwood, where κ is the Kappa number of the pulp or wood. The kinetics can therefore be estimated using the Kappa number in place of the lignin concentration, and Equation (3.3) can be rewritten as:

$$\frac{1}{\kappa_P \cdot yield} - \frac{1}{\kappa_W} = k^+_{AQ} A Q^{1/2} t \tag{3.5}$$

where κ_P and κ_W are the Kappa numbers of the pulp and the wood, respectively, and k^+_{AQ} equals $0.15 \cdot k_{AQ}$. If the yield is high, Equation 3.5 can be estimated by Equation (3.6):

$$\frac{1}{\kappa_P} - \frac{1}{\kappa_W} = k^+_{AQ} A Q^{1/2} t \tag{3.6}$$

It was found that Equation (3.6) works well for data covering bulk and residual delignification phases [49, 51].

Although they were researching a different kinetic phenomenon, Abbot and Bolker generated data that provide the best illustration that a change in AQ concentration in cooking liquor has no influence on its catalytic effect at constant AQ dosage on wood [49]. Figure 3.1 shows the Kappa number as a function of AQ charge on wood for two different liquor-to-wood ratios, 10:1 and 40:1, while all other conditions (i.e., hydroxide and hydrosulfide concentrations, time, and temperature) were held constant.

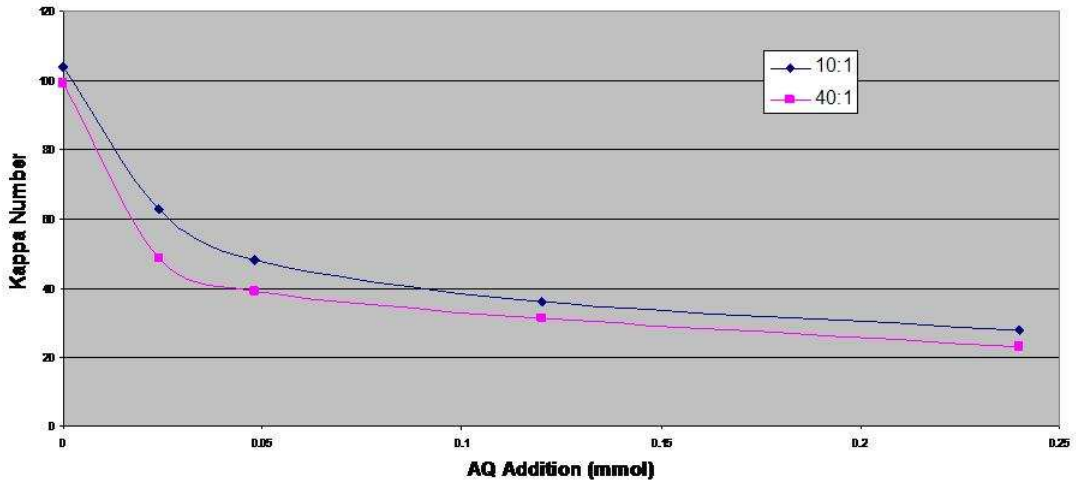

Figure 3.1: Plot of Kappa number versus AQ charge for different L/W ratios [49]. Notice that the higher L/W ratio has a lower Kappa No. for each AQ charge.

The pulps at higher liquor-to-wood ratio, i.e., 40:1, reached a slightly lower Kappa number at any given AQ addition. This may be due to the greater availability of caustic in the 40:1 case. The important point to take from this plot is that the trend is the same for both cases. Removing the effect of alkali availability, the addition of AQ has the same effect on delignification, and this cannot be explained by the effect of change in the concentration of AQ in the liquid phase. Increasing the L/W ratio by a factor of 4, from 10:1 to 40:1, with the same amount of AQ dosage effectively decreases the concentration of AQ in cooking liquor to 25% of the concentration at a 10:1 liquor-to-wood ratio. If AQ were always soluble in alkaline pulping, this concentration decrease would be evident in a decrease in AQ effectiveness, i.e., a flatter trend in the graph for the higher L/W ratio. The experimental results indicate otherwise.

This phenomenon is more clearly demonstrated when the data in Figure 3.1 are analyzed based on Equation (3.6). Figure 3.2 shows the plot of the inverse Kappa number

as a function of square root of AQ charge, which yields a straight line for each liquor-to-wood ratio. The straight lines indicate that these results can be described by the kinetic Equation (3.6). The slopes of the lines give the rate constants, k^{+}_{AQ}. The rate constant for 40:1 liquor-to-wood ratio is slightly higher than that for 10:1 liquor-to-wood ratio. This may also be due to the greater availability of caustic in the 40:1 case. However, the similar trend between the two plots confirms that the AQ concentration based on liquid volume is irrelevant to the AQ kinetics.

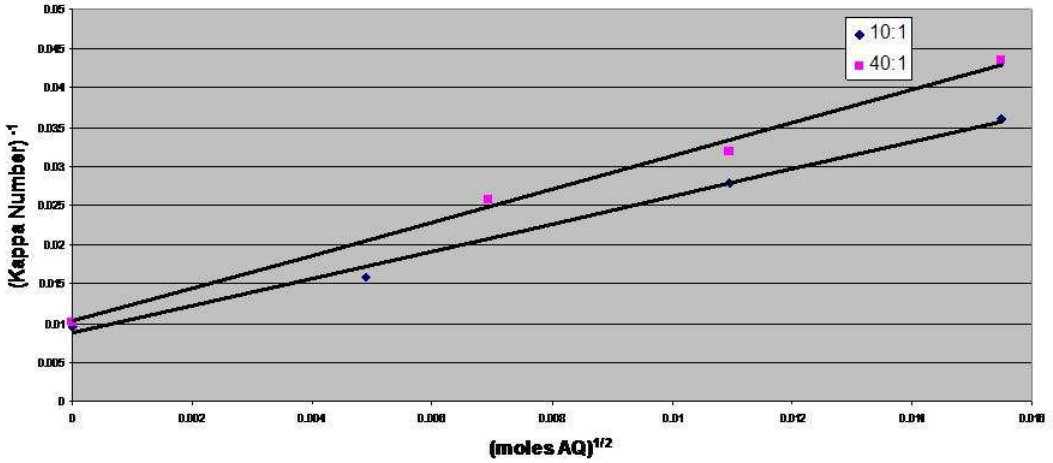

Figure 3.2: Plot of the kinetic effect of AQ addition on Kappa number at different L/W ratios [49]. Pulp made using liquor with an EA of 2.0*M* NaOH. Note the increase in Kappa number reduction rate for higher L/W ratio.

The Mechanistic Interpretation of the Kinetic Behavior

The fact that the data do not support the kinetics based on AQ concentration in liquid phase implies that another mechanism is occurring. The most likely explanation is that AQ is concentrated into the wood chips by some physicochemical effects. Therefore, the amount of AQ uptake by wood chips is a function of AQ available in the digester, and the kinetic rate of delignification is only affected by the amount of AQ

available in the wood chips. This explanation fits well with the kinetics based on AQ charge on wood rather than the concentration of AQ in the liquid phase. Therefore, the question of what phenomenon causes the AQ to concentrate in the wood chips arises.

Xylophilicity and Hydrophilicity

Werthemann gives one possible explanation in his discussion of the unique kinetics of AQ charge on wood [52]. His paper stated that AQ concentrated into wood chips due to the phenomenon that he dubbed the xylophilicity of AQ. This is a measure of the additive's affinity toward wood versus water in a pulping system. This is in contrast to the principle of hydrophilicity, which is a measure of the additive's affinity to water; i.e., an additive with higher hydrophilicity tends to remain mostly in the liquid phase. AQ has a low hydrophilicity, but not so low as to make it unable to move into the liquid phase. In comparison, anthraquinone-2-sulfonate (AQ-S) (a highly soluble derivative of AQ) has a very high hydrophilicity because of its high solubility. While in the liquid phase, AQ-S can diffuse out of the chip as easily as it can diffuse into the chip. This is used to explain the fact that AQ-S has much lower effectiveness than AQ does since AQ-S cannot selectively concentrate in the chips where it can be effective.

Although the concept of xylophilicity and hydrophilicity works well to explain the kinetic behavior of AQ and AQ-S, the experimentally measured AQ distribution in wood chips and bulk cooking liquor during a cook did not confirm it [53]. Actually, the fact that a large amount of AQ is released into bulk cooking liquor during the bulk delignification represents convincing evidence that xylophilicity is not the phenomenon responsible for the apparent behavior of AQ.

The "AQ Uptake" Mechanism

After analyzing many published reports on AQ kinetics, the catalytic mechanism on delignification, and the gradual decrease in the amount of AQ during alkaline pulping, the "AQ uptake" phenomenon is attributed to the "soluble and insoluble" cycle resulting from the redox reaction cycle.

Initially, the insoluble AQ particles are suspended in the cooking liquor. Some of the AQ could also be sitting on the surface of the chips. The AQ cannot enter the chips because the suspended particles are not dissolved and are unable to diffuse through the fiber wall. As the temperature rises, the AQ begins to be reduced to soluble AHQ by carbohydrates dissolving out into the liquor. The mobile AHQ molecules can then diffuse into the chip. Once inside the chip, the AHQ can react with lignin, becoming AQ again. Because AQ is insoluble, it becomes immobile, thus staying in the wood chips until it is reduced by carbohydrate reducing end groups. As more AHQ diffuses into the chips, more AQ is formed, and thus trapped in the chips. At this stage, the insoluble AQ is only reproduced from AHQ in the chips because most reactive lignin only resides in the chips. On a macro scale, it appears as though AQ is adsorbed or deposited into the wood chips, or one could even say that AQ is adsorbed by the lignin in wood.

The amount of AQ uptake by the wood chips is only a function of the amount of AQ available in the system, not its concentration. The amount of lignin depolymerization induced by AHQ depends on the amount that is taken up into the chip. Thus, the AQ effectiveness becomes proportional to its dosage on wood weight.

This AQ deposition process continues until the temperature reaches a point at which the delignification reaction rate is very high. As delignification continues, large

numbers of lignin fragments diffuse out of the chip into the liquor. These fragments are not completely depolymerized. Therefore, the AHQ in the chips can diffuse back out of the chips to react with the lignin in the liquor. At this stage, the apparent AQ accumulation in wood chips stops, and the AQ concentration in wood starts to decrease.

Experimental Confirmation

The AQ uptake mechanism proposed above is well supported by the study reported by Fleming et al. Polarographic analysis conducted by Fleming et al. shows that the concentration of AQ in the chips and liquor varies with time during the cook [53]. The data, obtained in soda-AQ cooking of black spruce chips, are presented in Figures 3.3 and 3.4. These plots display a very interesting picture of the location and oxidation state of AQ during the course of a cook.

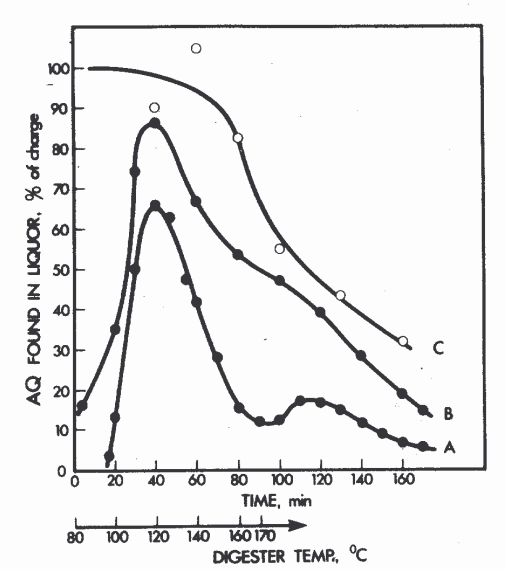

Figure 3.3: Distribution of AQ in pulping liquor as a function of both time and temperature [53].

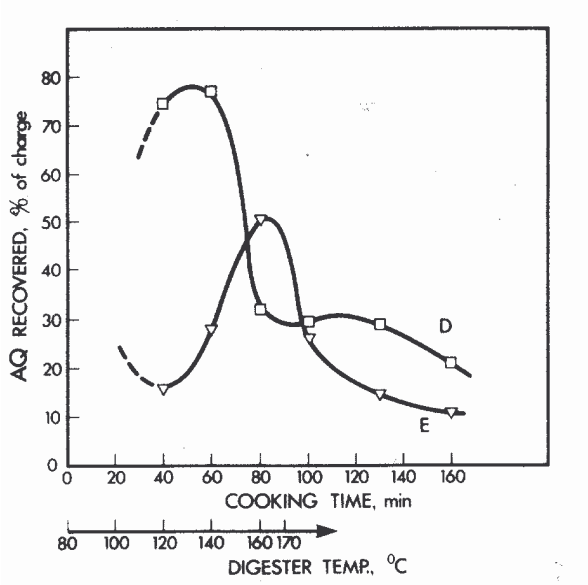

Figure 3.4: Distribution of AQ between free liquor (D) and wood chips (E) [53].

Curve A in Figure 3.3 represents the change in the concentration of reduced AQ forms ($AHQ^{=}$ and $AHQ^{\bullet}$) during the cook. Curve B represents the total AQ in the pulping liquor. Curve C represents the total AQ in both the liquor and the chips. Curve D in Figure 3.4 is the amount of AQ in free or bulk cooking liquor, while Curve E is the amount of AQ in wood chips [53].

Initially, there is very little AQ in any reduced form (AHQ) present in the system. As carbohydrates begin to dissolve into the liquor, these begin to reduce the AQ and render it soluble, accounting for the rise in Curves A and B. As the temperature rises, the rate of AQ-lignin reaction increases, causing the concentration of AHQ in the bulk liquor to decrease as AHQ diffuses into and is retained in the chips. This accounts for the drop in Curves A and B at above 120°C. Once cooking temperature is reached, Curve A, i.e., AHQ in bulk cooking liquor, increases somewhat, possibly because the AHQ diffuses out of the chips to react with the large amount of dissolved lignin. The widening gap

between Curves B and C in Figure 3.3 shows that AQ was depositing on the interstitial chip surfaces.

This is supported by the curves in Figure 3.4. At the approximate cooking temperature, total AQ (AQ and AHQ) reaches a maximum in the chips as shown in Curve E. At the same time, Curve D displays a minimum. The total liquor-to-wood ratio used in this study was 5:1 L/kg, and the liquor residing in wood chips when temperature reached 170^{o}C is about 1.5-2 L/kg wood; thus, bulk cooking liquor should be about 3-3.5 L/kg wood. Using these liquor distribution figures and the AQ distribution at 90 minutes in Figure 3.4, one can calculate that the AQ concentration in the liquor within the wood chips is 2.5-4 times higher than that in the bulk liquor. The only way for this to happen is that a large portion of the AQ within the chips is not in soluble form.

Another interesting aspect of these graphs is seen at the very beginning. Of the initial charge of AQ, about 85% is almost immediately deposited out of the bulk liquor, probably due to the high hydrophobicity of the AQ particles early in the cook. Some of this is on the walls of the digester, and some is on the chips themselves. Because of the much higher surface area of the wood chips, the majority of this deposition occurs on the chips. This extremely rapid deposition indicates that there is little external mass transfer resistance for AQ. Therefore, there is a very high external mass transfer coefficient, and the Biot number will be very high. This indicates that the diffusion of AQ species to the center of the chips will be limited mainly by the internal mass transfer in the chips.

The reaction between AHQ and lignin has been shown to be a single electron transfer (SET) reaction [33]. This report stated that the redox cycle was most likely between $AHQ^{\bullet -}$ (radical anion) and $AHQ^{=}$ (dianion). In contrast, the data presented here

suggest that the AHQ in the chips is oxidized all the way to the immobile AQ. Therefore, the data suggest that the redox cycle during alkaline cooking takes both pathways, between AQ and $AHQ^{\bullet-}$ and between $AHQ^{\bullet-}$ and $AHQ^{=}$. If the adduct mechanism is occurring, then the deposition of AQ is expected.

Figure 3.4 shows that in the later part of the cook, where a large amount of dissolved lignin has diffused into bulk liquor, the AQ distribution becomes similar to the liquor distribution inside and outside of the wood chips. This is because the redox cycle can take place also in bulk liquor; i.e., AHQ can react with the dissolved lignin in bulk liquor. The AQ distribution in this part of the cook also suggests that the concept of xylophilicity cannot be true since AQ is no longer "concentrated" inside the wood chips when the bulk liquor has a high enough concentration of dissolved lignin.

The large decrease in the total amount of AQ at the end of these cooks can be attributed to a couple of phenomena. First, the authors of the article from which these data are taken attribute the low AQ content to alkaline degradation of AHQ. They state that though AQ is resistant to alkali attack, AHQ is not as resistant, and can therefore degrade in hot alkali [53]. Another work attributes the decrease in the amount of AQ at the end of the cook to the formation of byproducts between AQ and lignin fragments [54].

AQ Efficacy in Pulping and Industrial Implications

Similar to other heterogeneous chemical reactions, the AQ mass transfer mechanism can have a significant impact on its catalytic effectiveness. Depending on how the pulping conditions are designed, the rate of AQ penetration, the AQ concentration in wood chips, and the reaction rate with lignin can be varied greatly. The

following are attempts to analyze how AQ mass transfer can affect the delignification rate and how its efficacy can be improved.

Soluble vs. Insoluble

Since AQ must be reduced to AHQ before it can diffuse into wood chips, and because it is in insoluble form after AHQ reacts with lignin in wood, the mass transfer of AQ to the center of wood chips is lower than completely soluble AQ derivatives, such as AQ-sulfonate (AQ-S). However, the slow mass transfer due to the insoluble AQ phase is a two-edged sword. Although it decreases the mass transfer rate of AQ, it can be beneficial in alkaline-AQ pulping. The insolubility of AQ causes AQ to be retained on the sites in the chip where it can be effective. If AQ remains soluble (i.e., in the forms of $AHQ^{=}$ and $AHQ^{\bullet}$) at all times in the cooking cycle, it would be able to diffuse out of the chip as readily as it can diffuse into the chip. This will make for speedier diffusion, and thus more homogeneous pulp, but the decreased concentration inside the chip where AQ is effective can be detrimental to its overall effectiveness. This analysis suggests that it may not provide any economical paybacks to develop or use completely soluble AQ derivatives.

Initial Insoluble Form

Although the completely soluble AQ derivatives may not provide an advantage over regular AQ, if AQ is initially in a soluble form, such as pre-reduced to AHQ, or a soluble AQ derivative, but can still undergo the soluble-insoluble redox cycle, it can be more effective in short heating-time cooks. This is because it eliminates the time required for the initial solubilization.

An article by Dutta and Biermann supports this effect. These researchers discuss the differences between 1,4-dihydro-9,10-dihydroxyanthracene (DDA, also known as soluble AQ or SAQ) and AQ. Their data show that DDA is a more effective additive than AQ. DDA is soluble in aqueous solution. Its solution can be easily dispersed into the white liquor. Dutta and Biermann used an "instantaneous" or very short heating time to the final cooking temperature by preheating the hot oil bath to the cooking temperature before the bomb digesters were placed into the bath [55]. The short rise to cooking temperature does not allow AQ to be reduced by dissolved carbohydrates in the liquor before the alkali in the digester reacts with the wood components. Since it cannot be reduced until later in the cook, by the time AQ has diffused into the chips it would be too late to provide the catalytic benefits. However, Dutta and Biermann's results would be applicable to digesters with very short heating times, e.g. vapor phase cooking using direct steaming.

The work by Nomura and Nakamura supports these results. The researchers showed that DDA and tetrahydroanthraquinone (THAQ, the oxidized form of DDA) both were more effective at improving yield and delignification than AQ [56]. However, they too used a very short rise-to-temperature period that did not allow the AQ in the system to reduce and dissolve. Therefore, the experimental set-up limited the mass transfer of AQ, and therefore its effectiveness.

Other researchers, however, found conflicting results: that AQ was at least as effective as DDA. Pekkala compared THAQ to AQ and found it to be only 95% as effective as AQ [57]. In his experimental design, Pekkala allowed for a rise-to-temperature time of 105 minutes. This gave enough time for the AQ to be reduced to the

soluble state by the carbohydrates. Under these circumstances, the initial mass transfer limitation of AQ is reduced. Pekkala's and Dutta and Biermann's results confirm that mass transfer could play an important role in making AQ more effective. If AQ is supplied in a soluble form, it can be more effective in the pulping processes with short heating time.

Initial Presence of Dissolved Lignin in Cooking Liquor

One important phenomenon proposed in the present report is that the "AQ uptake" by the wood chips results from the oxidation of AHQ to insoluble AQ by lignin in wood. However, if there is a large amount of dissolved lignin in the bulk cooking liquor, the redox cycle can take place in the bulk liquor as well. The "AQ uptake" by wood chips would not happen to a large extent, and thus the AQ concentration in wood chips would be about the same as in bulk liquor. Therefore, the overall AQ effectiveness would be lower than that when dissolved lignin is not present in the initial cooking liquor.

Some studies performed on AQ effectiveness in rapid displacement heating (RDH) cooking provide the supporting evidence for the above suggestion. It was found that when AQ was added with warm black liquor and hot white liquor, it provided little catalytic effect on delignification. When AQ was added with hot black liquor, delignification was accelerated [46, 47]. The overall effect, however, was less than that seen in conventional kraft cooking. The large amount of dissolved lignin in the hot black liquor can react with some of the AQ.

It was observed in some mill trials that when AQ was added with the black liquor rather than white liquor in conventional batch cooking, its effectiveness was lower. The original thinking of adding AQ with black liquor was that the dissolved sugar molecules

in black liquor would reduce AQ to AHQ more quickly, so that AQ would be able to penetrate wood chips faster. There is no evidence that such thinking is wrong. The likely explanation is that the dissolved lignin has "short-cut" the redox cycle in bulk liquor rather than in wood chips.

The above discussion suggests that the effectiveness of AQ will be impaired when it is added to a cooking environment containing a large amount of dissolved lignin, such as all phases in RDH-type cooking and in the middle of continuous cooking.

Concluding Statements

The "AQ uptake" mechanism proposed here explains the catalytic effect of AQ in terms of the kinetics, chemistry, and physical properties of AQ and wood. The proposed mechanism bridges the gaps between prior conclusions that previously could not be explained. It is probable, from this analysis, that AQ is concentrating inside the chips during the cook to a higher concentration than is present in the bulk liquor. This may explain some of the differences in AQ efficacy reported in the literature, as the conditions of the cook can impact this concentrating effect.

Exploring and understanding the AQ diffusion mechanism could lead to a fundamental shift in the way that AQ is utilized in pulping operations. Improved understanding of the role of mass transfer could lead to methods to improve the use of AQ to increase its effectiveness. Therefore it is important to explore the means by which AQ transfers into wood chips.

CHAPTER 4

MODEL SYSTEM FOR AQ PULPING

In order to more fully explore the means by which AQ transfers into a wood chip, a model system was used. The Nafion membrane chosen for the model is similar to a wood chip in caustic media in that both have a negative surface charge. This is important because the transferring species, according to the "AQ uptake" mechanism described above, is the negatively charged AHQ (either the radical anion or dianion). Using a neutral or cationic membrane would be a poor choice for a model system. This work is reproduced here in modified form from previously published works [58, 59].

Membrane Mass Transfer

It has been shown previously that high ionic strength solutions can allow the permeation of anions through an anion exclusion membrane by swamping the membrane with cations, thus overcoming the Donnan effect [60-62]. Thus, a small percentage of the anion content can diffuse through the anionic membrane. This is an inefficient separation, but it is useful in development of analytical technology for separating a small, detectable, amount of low molecular weight anions from a complex liquid matrix containing high molecular weight substances. A previous paper reported on a flow analytical system which uses such an anion exclusion membrane system to separate hydrogen sulfide ions from larger molecular weight species in wood pulping spent liquors [63]. This system was designed for online measurement of the sulfide content of liquors .

Later data show that there is an inverse relationship between the penetration efficiency of an anionic compound in a tubular Nafion membrane and the molecular

weight of that compound [64]. Here, penetration efficiency is defined as the ratio of the concentration in the acceptor stream to the concentration in the donor stream. The authors present a large range of molecular weights and ionic charges over which this relationship holds. Some of their data is presented in Figure 4.1.

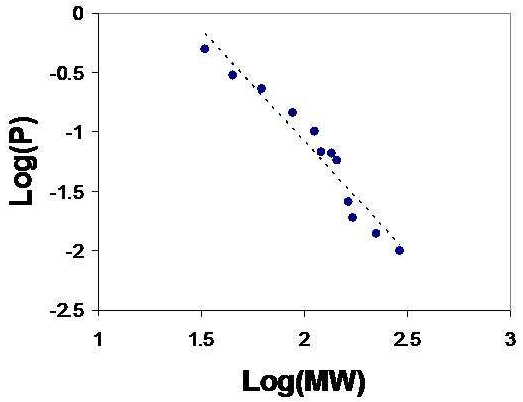

Figure 4.1: The log–log plot of penetration efficiency vs. molecular weight [64]. Data from flow rate of 0.5 mL/min and temperature of 21°C for inorganic and organic molecules with molecular weight (MW) ranging from 33 to 290 g/mol.

However, other studies demonstrated an exception to this behavior. These researchers observed that anthrahydroquinones (AHQs) do not permeate the membrane at moderate concentrations [65, 66]. Because such a variety of compounds can permeate the Nafion tubing, the lack of permeation by AHQs is quite interesting.

AQ itself cannot permeate the polymer membrane because it is insoluble in the selected media. However, the reduced form, AHQ, is soluble. In order to quantify the amount of AQ present in a solution, it is often easier to reduce the AQ in the solution to AHQ, which has a spectral absorption in UV-vis. range as shown in Fig. 4.2, and determine the concentration using a spectrophotometer. However, when other compounds, such as lignin in spent pulping liquors (black liquor), that absorb light in the

same region as AHQ (also shown in Figure 4.2) are present, it becomes very difficult. Therefore, a method which separates the AHQ from the other compounds is desirable. This is the basis for a membrane separation-based analytical system such as that described by Danielsson and Yang [64].

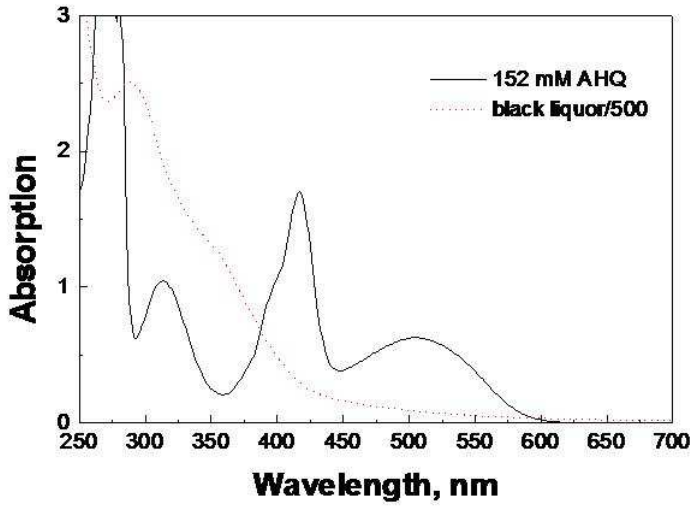

Figure 4.2: UV-vis. spectra of anthrahydroquinone (AHQ) and a diluted (1/500) black liquor.

Because reduced anthraquinones are excluded by the Nafion membrane at moderate concentration, a pre-reduction of the AQ is deleterious to quantification. It has been observed, however, that the presence of a strongly reducing compound such as sodium dithionite in the acceptor stream produces a signal for AHQ when the polymer tubing is placed in a suspension of AQ particles in base solution. The present work was undertaken to explore more deeply this observed behavior.

Experimental

Chemicals and Sample Preparations

All chemicals used in the experiment were from commercial sources. Distilled water was used in solution preparation.

Membrane Permeation Study

The apparatus and procedures were previously developed by Yang, et al. for determining AQ species concentrations in pulping liquors [65]. The schematic diagram of the flow analysis system is shown in Figure 4.3. The acceptor stream (10 mmol/L $Na_2S_2O_4$ + 0.1 mol/L NaOH solution) was pumped through a tubular membrane, Nafion 811 (Perma Pure, Toms River, NJ, USA), by a peristaltic pump (PR-1, Rainin, Woburn, MA, USA) at a flow rate of 0.5 mL/min, while AQ or its derivatives in the sample liquor (donor solution) permeated through the membrane into the carry stream to constitute the acceptor stream. The membrane tubing was 46 cm long and was placed in a 20-mL sample vial that was submerged into a water bath heated to a controlled temperature of 90^{o}C throughout the experiment to achieve a constant and higher transport rate through the membrane. The acceptor stream flows through a cooling unit to bring the temperature of the flow down to room temperature. The acceptor stream finally reached the flow cell with 1 cm optical path length of a spectrophotometer (HP-8453, Agilent Technologies, Palo Alto, CA, USA). Absorption spectral signals in UV-visible range were continually recorded by the spectrophotometer.

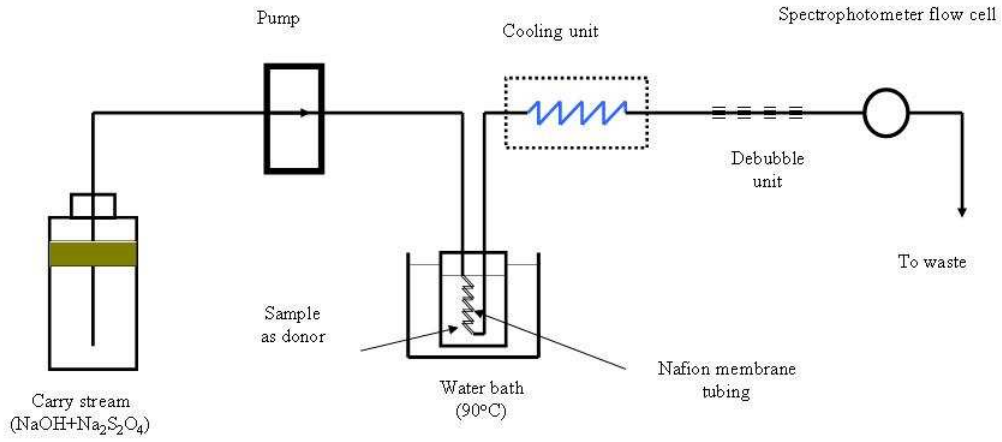

Figure 4.3: Schematic diagram of the flow analysis and membrane interface system [65].

AQ-Wood Lignin Analysis

A scanning laser microscope (SLM) was used to measure approximate particle size distribution of AQ suspended in caustic solutions with and without lignin present. The SLM measures the chord length of suspended particles by measuring the duration of backscattered light. This technique does not yield absolute particle size, but it is useful for observing trends and changes in the particle size distribution [67].

Results and Discussion

Hydroquinone Permeation

Initially it was thought that AHQs could not penetrate the membrane because of the high molecular weight. However, Danielsson and Yang showed that molecules of molecular weights higher than AHQs could penetrate [64]. Therefore, it was hypothesized that the electronic structure of the AHQs could have an impact.

In order to explore this, the first experiment used hydroquinone (p-dihydroxybenzene) as a model for AHQ. The penetration of the hydroquinone was

compared to that of phenol. These two compounds have similar molecular weights and structures as shown in Figure 4.4. The main difference is in the electronic configurations. The phenoxy anion has three resonance structures while the hydroquinone dianion has six.

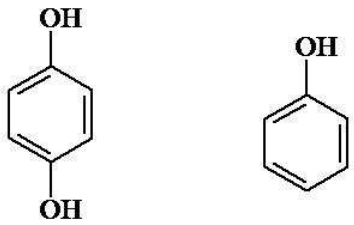

Figure 4.4: Chemical structures of hydroquinone (left) and phenol (right).

Based on the data from Danielsson and Yang [64], the penetration should differ only by the ratio of the logarithms of the molecular weights. In this case the ratio is 0.967 (phenol to hydroquinone); i.e., the penetration of hydroquinone should be approximately 97% that of phenol. However, the results show that the observed penetration of phenol is approximately 3.6 times that of hydroquinone. It appears from this that the quinone structure is special. This could be due to either the resonance structures discussed above, or the bifunctionality of hydroquinone.

It has been shown previously that hydroquinones elute from gel permeation columns earlier than their molecular weights would suggest [68]. It was stated in this paper that this is possibly due to the association of hydroquinone hydroxyl groups with the solvent. However, it may also be possible for the hydroquinones to associate with other hydroquinone molecules in solution, thus increasing the apparent molecular weight. This in turn could have an impact on both gel permeation and membrane penetration.

Soluble Anthraquinones

It was observed previously that anthraquinone-2-sulfonate (AQ-S) ions can permeate the membrane, but AHQ and anthrahydroquinone-2-sulfonate (AHQ-S) cannot permeate the membrane at the same concentration [65]. Since that work, it has been observed that the presence of a strongly reducing compound, such as sodium dithionite, in the donor solution decreases the observed permeation AQ-S in the membrane system. The decrease is due to some of the reducing compound converting some of the AQ-S into AHQ-S. The chemical structures of anthraquinone-2-sulfonate and anthrahydroquinone-2-sulfonate are shown in Figure 4.5. The observed results are summarized in Table 4.1.

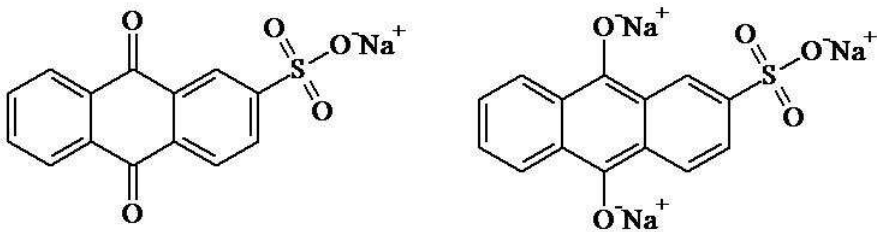

Figure 4.5: Chemical structures of anthraquinone-2-sulfonate (left) and anthrahydroquinone-2-sulfonate (right) in basic medium.

There are a couple of possible explanations for this observed behavior. First, the formation of AHQ-S simply may decrease the overall amount of available AQ-S for penetration. Second, the formed AHQ-S may associate with both AQ-S and other AHQ-S to decrease the available AQ-S even more. It has been previously shown that aromatic molecules such as AHQ-S can form charge-transfer complexes with electron-acceptor molecules such as quinones [69]. It is uncertain from these experiments which of these possible explanations is correct.

Table 4.1: Summary of observed behaviors of AQ and AQ derivatives; (+) indicates a signal detected at the spectrophotometer, (-) indicates no signal.

Sample composition in Donor (NaOH medium)	Acceptor	
	NaOH	Dithionite + NaOH
AQ-S	+	+
AHQ-S	-	-
AQ*	-	+
AHQ	-	-

* AQ initially as suspended solids in donor stream.

Regardless of the mechanism, it is true that AHQ-S does not readily pass through the membrane at moderate concentrations. This also holds for AHQ under similar circumstances, as demonstrated in Figure 4.6 [66]. In this experiment, dithionite was added to an AQ suspension while the experiment was being run. As AQ was converted to AHQ in the bulk solution, the signal from the acceptor stream drops to almost zero. Since the donor stream was open to the air in this experiment, the AHQ readily oxidized to form AQ and the signal returned.

Experimentation also showed that AHQ-S transport across the membrane interface is enabled, i.e. becomes measurable, at very high concentrations. When the concentration of AHQ-S is near saturation, a measurable amount of AHQ-S is observed passing through the membrane. It is hypothesized that a very high concentration of AHQ-S contains both a high amount of associated AHQ-S unavailable for membrane penetration and a high amount of non-associated, and therefore available, AHQ-S in equilibrium with the associated specie. A similar behavior is observed for AHQ.

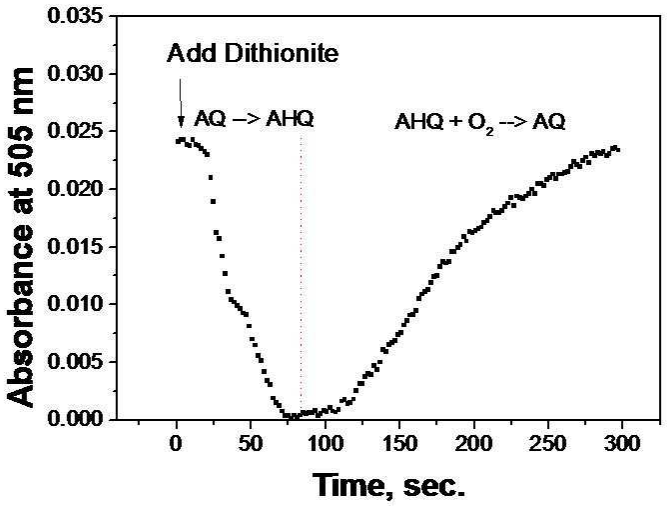

Figure 4.6: Figure from Yang, et al. showing the inability of AHQ to permeate the Nafion membrane interface [66].

Anthraquinone Transport Mechanisms

Because AQ is insoluble in aqueous solution, it cannot pass through the membrane unmodified. However, it has been observed that when a strongly reducing specie, such as dithionite ion, is present in the acceptor stream a measurable amount of AHQ is found in that stream, as displayed in Table 4.1. Therefore, based on the above observations of AHQ and AHQ-S, a very high concentration of non-associated AHQ must be formed at the surface of the membrane to enable penetration.

Based on these observations, the following mechanism is presented. First, suspended particles of AQ migrate to the surface of the membrane tubing due to stirring or Brownian effects. There, the hydrophobic AQ particle adsorbs on the membrane surface. Meanwhile, because of the high concentration of sodium ions in both the donor and acceptor solutions, some dithionite ions from the acceptor can overcome the Donnan exclusion and pass through the membrane to the donor side. Here the ions react with AQ adsorbed on the surface, forming AHQ. Depending on the extent to which the membrane

surface has been covered by AQ particles, some of the AHQ can diffuse out into the bulk solution. However, much of the AHQ formed between the AQ particle and the membrane surface cannot move, initially, due to blocking by the AQ crystal and association of AHQ with the water and other AHQ molecules. Thus the concentration of AHQ at the membrane surface increases as more dithionite reacts with the AQ.

Once a high enough surface concentration is reached, measurable amounts of AHQ begin to pass through the membrane, due to the swamping by sodium ions. The surface AHQ concentration then remains at equilibrium as AHQ is formed by dithionite and some AHQ penetrates the membrane. The mechanism is displayed schematically in Figure 4.7.

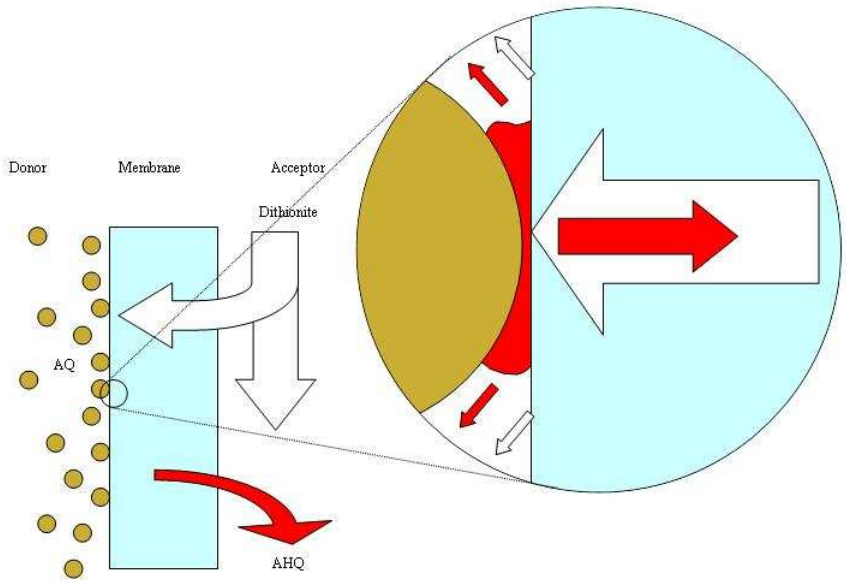

Figure 4.7: Schematic diagram of proposed AQ membrane transfer system.

AQ is assumed to be completely insoluble in the above mechanism. However, if there is a slight solubility, another possibility arises. The actual value is unknown so we will use 10^{-12} as the order of magnitude of the concentration in bulk solution for

demonstration purposes. If the solubility in the membrane is much higher than that in the bulk solution (e.g. giving a concentration in the membrane on the order of 10^{-6}) then the partition coefficient is very high (on the order of 10^{6}). If this were the case, the membrane will act as an AQ "sink" pulling any dissolved AQ out of the bulk solution. Then because of the concentration gradient between the membrane and the acceptor stream, AQ will flux into the acceptor stream.

However, Table 4.1 shows that without the presence of dithionite, no AQ is observed to pass through the membrane. If this mechanism were true, then dithionite would not be required for membrane penetration. Therefore, this alternate mechanism is discarded on the proof of experimentation.

The Role of Wood Lignin

When wood lignin is added to the donor side, a much higher signal is produced. As shown in Figure 4.8, the liquor containing pure alkaline lignin (70g/L lignin in 1.5*M* NaOH) had an order of magnitude greater response than the pure sodium hydroxide solution (1.5*M*). This indicates that the lignin somehow enhances either the penetration of AHQ into the membrane or the amount of surface area of the membrane covered by the AQ.

Lignin could enhance the penetration of AHQ by interfering with the "association" between AHQ molecules, thereby increasing the concentration of available non-associated AHQ molecules for penetration. However, it could also enhance the surface area covered by AQ. Lignin has been shown previously to have a high dispersion power [70]. The lignin may act as a dispersant, creating smaller AQ particles that can better cover the membrane surface, thus making more AQ available to the membrane

surface. Some evidence supporting this theory is presented in Figure 4.9. This plot shows that when lignin is present, the particle size distribution is shifted to the lower sizes.

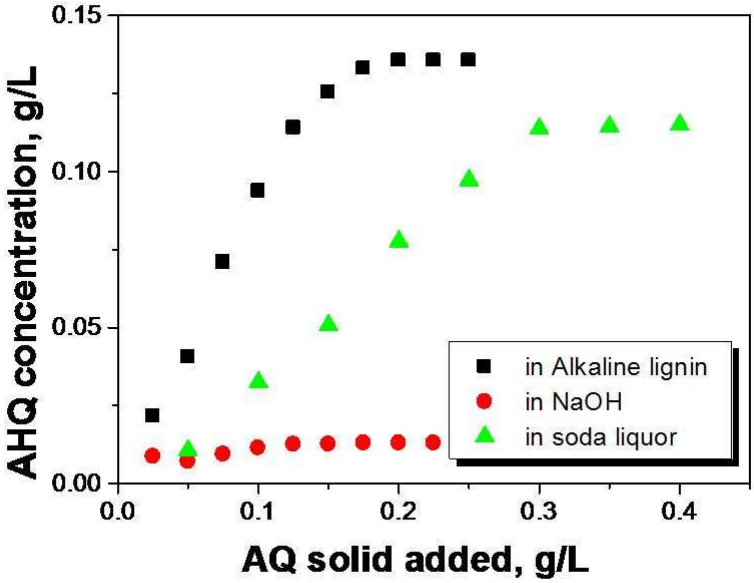

Figure 4.8: AHQ concentration detected in the acceptor stream for various liquor compositions at 90°C.

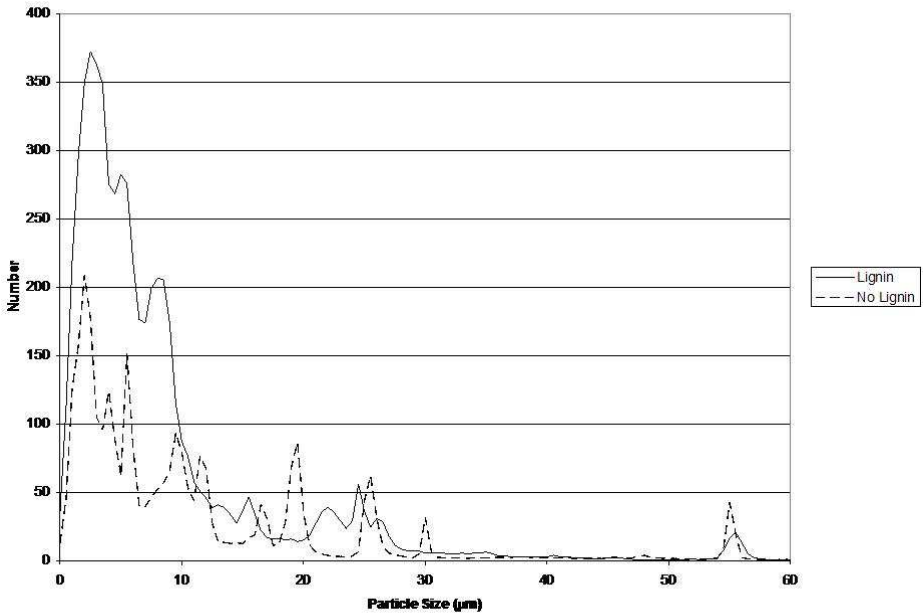

Figure 4.9: Particle size distribution of AQ in suspension with and without lignin present. Lignin decreases the average particle size of AQ in suspension.

Although lignin enables enhanced permeation of the membrane, AQ has been shown to have less effect in processes that use black liquor for impregnation [46, 47]. It is the third line in Figure 4.8 that can explain this discrepancy.

The response of AQ in a soda black liquor (H = 1000) is lower than that in the alkaline lignin solution when adding the same amount of AQ solids. This is due to the significant amount of carbohydrates that soda liquor contains, which can convert a part of the AQ into AHQ in the bulk solution, rather than at the membrane surface. Again, AHQ cannot pass through the polymer membrane at the low concentrations present in the bulk solution. The response of AQ is also limited by the concentration of the dissolved lignin in the soda liquor. Thus, it is not the lignin that harms AQ efficacy in displacement style cooking, but the carbohydrates.

Concluding Statements

Anthraquinone displays a very interesting mass transfer behavior in anionic membrane systems. Through adsorption and surface reaction, a measurable amount of AHQ can permeate the polymeric system. The use of surfactants and dispersants such as dissolved wood lignin can lead to higher penetrations of the polymer membrane system. This model system is similar to a wood chip during pulping, and therefore, the mechanism described here may indeed be the method by which AQ enters into the wood chip.

CHAPTER 5

MODEL SYSTEM BEHAVIOR IN PULPING

The mass transfer behavior of AQ in a model system has been here described. In this system, there are two major steps required for AQ permeation of an anion exclusion membrane. These are surface contact and surface reaction. In the previous work, it was suggested that this mechanism could be similar to what happens in alkaline pulping with AQ.

The purpose of this work is to explore pulping data to identify the steps above in pulping systems. Validating these steps can lead to a better understanding of alkaline-AQ pulping systems. This could then lead to knowledge of how different conditions affect AQ efficacy in pulping.

Surfactants and AQ Particle Size Effects

Many researchers have studied the use of surfactants in alkaline pulping and oxygen delignification [71-79]. It is generally agreed that surfactants can increase the solubility of large lignin pieces, thereby improving delignification [80, 81]. This can result in chemical savings as less caustic is required to remove the lignin. It is possible that the surfactant also increases the rate of alkali uptake by the wood, but it has been shown that the use of surfactants actually decreases the affinity between caustic and wood [71].

Other researchers have studied the use of surfactants specifically in alkaline-AQ pulping experiments [82-87]. It has been shown that the use of surfactants with AQ can improve pulping results over the combined individual effects [85]. The relationship between surfactants and AQ is therefore synergistic. It has been stated that this synergy

is due to enhancing the permeation of AQ into wood chips, possibly by enhancing the solubility of AQ in the system [87]. It has also been suggested that the surfactant improves AQ selectivity while increasing white liquor penetration [86].

In the preceding work, it was shown that the presence of wood lignin increased the permeation of AQ in the membrane. It was suggested at the time that alkaline lignin could be working as a surfactant, due to its reported surfactant ability. Another possibility, that the lignin provided more locations for AHQ oxidation, was also put forward. Both mechanisms would lead to the same result: smaller AQ pieces. This was supported by particle size distribution data (see Figure 4.8). The decrease in AQ particle size then leads to a higher surface area of the membrane in contact with AQ pieces.

It is suggested, therefore, that the surfactant in the pulping experiments is behaving in a similar fashion to the lignin in the membrane study. The data from the particle size distribution study showed that even without a reducing agent, the surfactant ability of the lignin solution was enough to considerably decrease the average particle size of the AQ.

Thus it is probable that the surfactant in the pulping studies is neither enhancing solubility nor directly enhancing penetration efficiency, but is in fact dispersing the AQ more effectively to cover more surface area of the wood chips. Previous work has also concluded that surfactants work to increase AQ dispersity [82]. More surface area covered increases the permeation rate [58], thereby improving the efficacy of AQ. This then accounts for the synergy in alkaline surfactant-AQ pulping.

It is this synergy itself, though, that lends support to the veracity of the mechanism revealed in the membrane experiments in pulping. Surface contact is an

obviously important step in the pulping process. Other methods of improving surface contact should also improve AQ efficacy.

A recent study examined AQ obtained from different manufacturing techniques [88]. One sample (AQ-F) was taken from the Friedl-Crafts substitution of phthalic anhydride and benzene with subsequent cyclization via dehydration. A second sample (AQ-A) was taken from the direct oxidation of anthracene. The third sample (AHO) was from the waste products from the oxidation of anthracene, and included anthraquinone as well as impurities such as phthalic anhydride, phenanthrene, anthracene, and other compounds [89].

One of the main reported differences between these samples was the specific surface area of the AQ model. The AQ-F had four to eight times more surface area than the other two. It also displayed improved yield and delignification over the other two. The researchers also found that exposing the AQ-A and AHO to an ultrasonic field increased the specific surface area of these compounds. This treatment increased the specific surface area by about 20% for AQ-A and by about 250% for the AHO model as shown in Table 5.1 [88].

Table 5.1: Influence of AQ model on the composition of pulp from pine sawdust [88].

Indices	AQ Model					
	-	AQ-F	AQ-A		AHO	
			-	US-field	-	US-field
Specific Surface Area, m^2/g	-	4.0	0.9	1.1	0.5	1.6
Yield, % OD Wood	49.0	49.1	49.0	49.1	49.0	49.1
Residual Lignin, % OD Wood	15.3	8.2	10.2	8.6	9.2	8.4
Hemicellulose, % OD Wood	7.2	15.4	9.3	10.5	11.7	15.1

These ultrasound-treated compounds were then used in pulping, and the results were similar to those of AQ-F. Yield and hemicellulose content were increased over untreated chemicals and residual lignin was decreased. The authors indicate that the increase in catalytic activity for the AHO model is not due solely to its increased specific surface area, but also due to the impurities present somehow increasing the reduction rate of the catalyst [88]. However, it is more likely that the impurities in the AHO sample contributed to the large increase in specific surface area, and it is this increase that has made such an improvement in pulping result. This indicates even more strongly that the particle size of AQ impacts the mass transfer, and therefore the results, in pulping.

Bulk versus Surface Reduction

The second step identified in the membrane study is surface reaction. Adding a reducing compound to the donor solution caused the permeation rate of AQ and AQ-S to decrease rapidly [58]. Only when the reducing compound was in the acceptor solution was any AQ detected at the detector.

In one pulping experiment, glucose was added to a soda-AQ cook of pinewood chips. Originally, this was done to try to aid initial reduction of AQ and enhance penetration and diffusion by maintaining AQ in soluble form. However, according to the mechanism proposed, this should have a detrimental effect on pulping. The results are shown below.

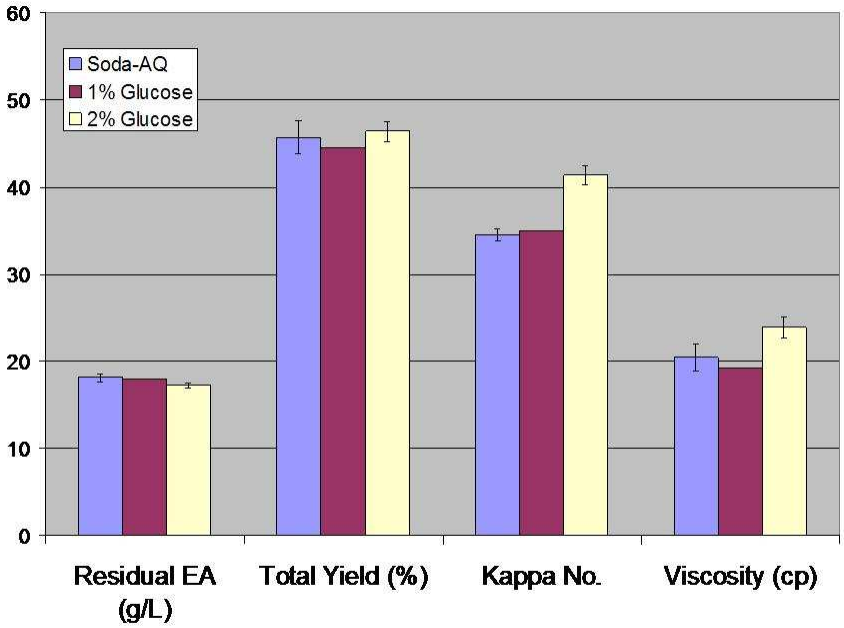

Figure 5.1: Effect of glucose on soda-AQ pulping results. Error bars are 90% confidence interval. Columns without bars are from single data point.

The experiment was conducted with 100g oven dry (OD) wood in a 1L rotating digester (Aurora) at a maximum temperature of 170^{o}C with a ramp time of 90 minutes. The cooks were conducted with effective alkali (EA) of 18% and an AQ charge of 0.1% on OD wood. For the glucose experiments, glucose at 2.0% on OD wood was added at the beginning of the cook. All cooks were completed at an H factor of 1600.

The presence of glucose in the cook is detrimental to the resulting pulp. The rise in residual EA indicates an overall slowing of the pulping reactions, as less caustic has been consumed. This is unexpected, since the addition of glucose should increase the consumption. The drop in yield with a simultaneous rise in the kappa number over the soda-AQ cook shows that the process is much less selective than soda-AQ. The one positive is the increased viscosity of the pulp, indicating some improvement in carbohydrate length.

One explanation for these changes is that glucose is reducing the AQ in the bulk phase. This is similar to placing sodium dithionite in the donor solution of the membrane experiment. Reduction in the bulk phase decreases the permeation into the membrane. Here the effect is similar.

However, the glucose-AQ reaction is relatively slow [90], so the results may be due to the consumption of alkali by the glucose. This would show up as increased yield, kappa number, and viscosity. The increase in residual EA and decrease in total yield belies this explanation. If glucose were consuming the alkali, then the residual EA should be lower, not higher. In order to clarify this, a faster reducing agent was used.

This same experiment was conducted with sodium dithionite as the reducing species. The results (Figure 5.2) are remarkably different. The results differ depending on the dosage of sodium dithionite. Interestingly, the presence of a low dose of sodium dithionite in the soda-AQ cook favors the carbohydrate stabilization, to the slight detriment of delignification. The yield and viscosity increase, with a slight increase in the Kappa number. This is not expected, based on the chemistry of AQ pulping. Since the presence of sodium dithionite should keep the AQ in a reduced state, thus enhancing delignification at the cost of carbohydrate stabilization. This is what happens at the highest sodium dithionite dose. The middle dosage falls between the two others.

It should be pointed out here that these experiments were conducted in the presence of oxygen. This means that oxygen in the system could immediately oxidize any AHQ formed by reaction with these reducing agents. This could then lead to the formation of several very small AQ particles, effectively decreasing the average AQ

particle size and spreading out the AQ across more chip surface area, much the same as a surfactant, as previously discussed.

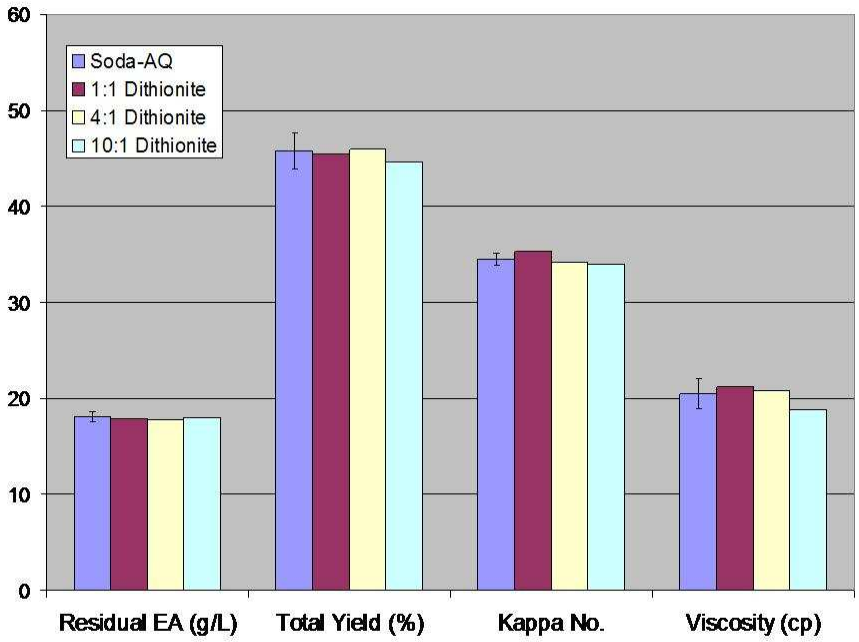

Figure 5.2: Effect of sodium dithionite on soda-AQ pulping results. Error bars are 90% confidence interval. Columns without bars are from single data point.

To test the hypothesis that reduction and reoxidation will create smaller AQ particles, a small experiment was performed. Anthraquinone powder was dispersed in a caustic solution (pH = 12.4) and analyzed using the scanning laser microscope used in the particle size analysis previously. After a time, sodium dithionite solution was added to begin AQ reduction. The results are shown in Figure 5.3.

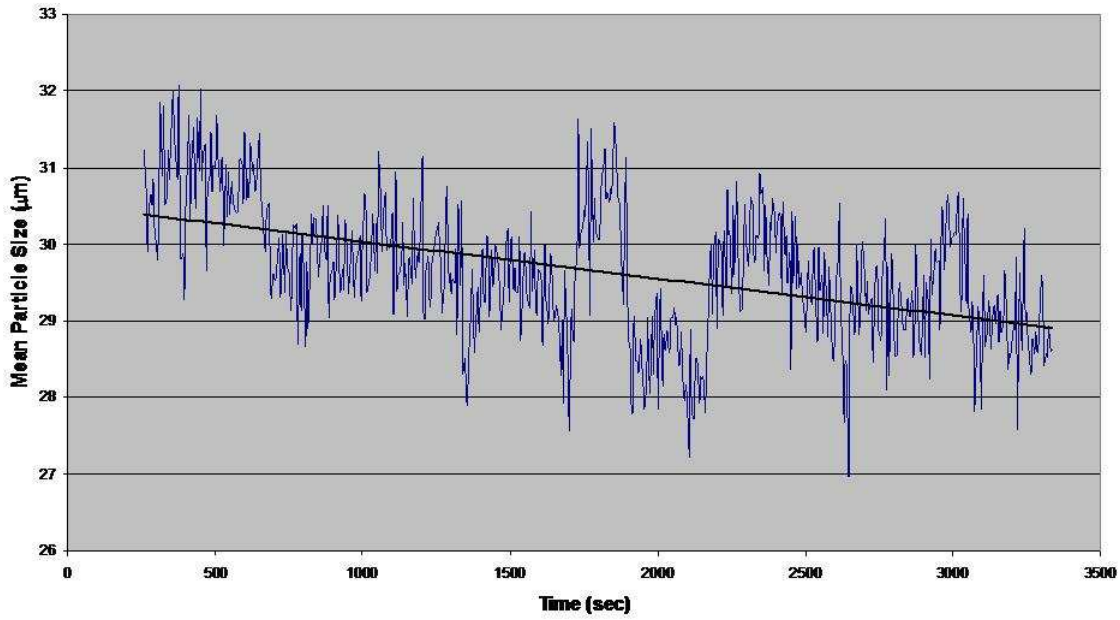

Figure 5.3: Particle size changes due to AQ reduction and reoxidation.

Though there is a considerable amount of noise from the experiment, there is a downward trend in the mean particle size. Regression analysis shows this drop in particle size is significant. Therefore, the null hypothesis that there is no change in particle size is rejected with 99.9% confidence.

At higher dosages of sodium dithionite, this reoxidation effect is limited because of the very high concentration of dithionite. Many of these small AQ particles will be readily reduced once again, keeping it away from the wood chips. This pushes any reactions that do occur toward more delignification, as shown in the Kappa number drop, at the detriment of carbohydrate stabilization (viscosity drop).

It is also possible for sodium dithionite to directly impact pulping without the reactions with AQ. It has been shown that sodium dithionite can alter the results of pulping on its own [91]. Sodium dithionite is also often used in reductive bleaching

processes for mechanical pulps and recycled paper [92, 93]. The following graph gives some indication of the effect that sodium dithionite has on soda pulping.

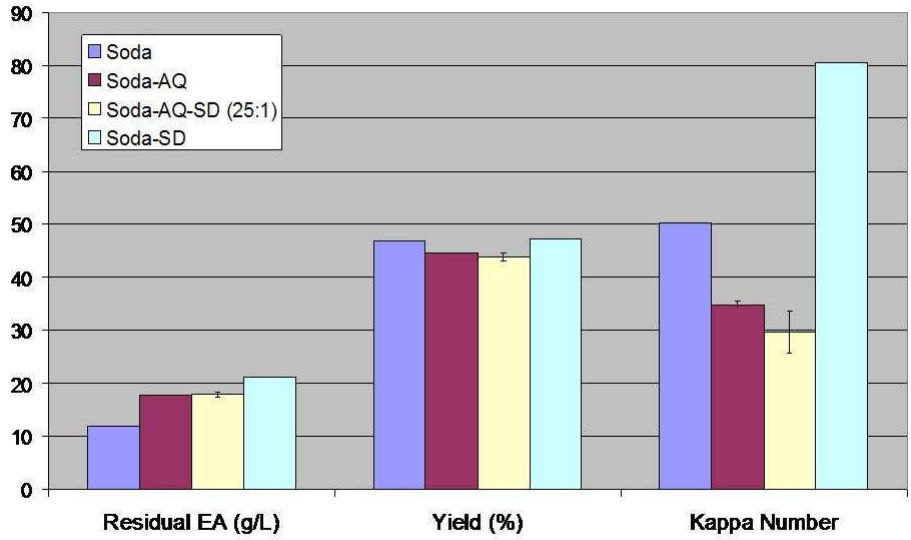

Figure 5.4: Effect of sodium dithionite on soda pulping in the presence and absence of anthraquinone. Error bars are 90% confidence interval. Columns without bars are from single data point.

The presence of sodium dithionite has almost no impact on the total yield, but it has a significant impact on the Kappa number. The sodium dithionite aggressively slows delignification in the absence of AQ. Therefore, it is evident that the improvements in pulping are due to the action of sodium dithionite on AQ, rather than directly on wood.

Thus the pulping data are consistent with the proposed mechanism. Surface reaction is important in delivering AQ to the inner chip surfaces. Bulk reduction will tend to keep permeation of the chips lower, as in the membrane study. Validating this, the mechanism from the membrane study can be amalgamated with the earlier "AQ uptake" mechanism to give a more complete analysis of the mass transfer behavior of AQ during pulping.

Mechanism

First, AQ must contact the outer surface of a chip. The greatest effect of AQ is obtained by the greatest surface coverage. As the literature data show, surfactants can increase AQ dispersity, and thus improve AQ efficacy. This could also be obtained by adding a small amount of a fast reducing agent early in the cook, as was done with sodium dithionite in the pulping experiments.

Next, the AQ reacts at the surface with carbohydrates in the wood chip. This reduces the AQ along the surface of the chip, creating localized, very high concentrations of AHQ. This is the diffusing species. The AHQ then permeates the chip according to Fick's laws. However, the wood chip is a reactive membrane. AHQ that is diffusing will react with in situ lignin, causing AQ to precipitate on chip surfaces. Some of the AQ will react once again with carbohydrates and continue to diffuse, but it is the precipitation of AQ inside the chip that allows for the concentration of AQ in the chip to rise above that of the bulk solution.

This ensures that most of the AQ-lignin-carbohydrate redox cycle occurs in the wood phase, rather than in the bulk liquor. The effectiveness of AQ to such a redox cycle will decrease when the formed AHQ exits the chip into the bulk solution. AQ will lose its functionality in later stages of the pulping process since a large amount of dissolved lignin and carbohydrates passes into the process liquor, thus allowing the redox cycle to take place in the liquor phase rather than in the wood phase. The efficacy of AQ pulping is diminished by side reactions that consume AQ [53, 94, 95]. However, the effectiveness of the remaining, un-reacted, AQ is also reduced due to the liquor phase redox cycle [59].

Concluding Statements

Thus, the mechanism determined for the membrane system is shown to be active in the alkaline pulping of wood with AQ. Alkaline-AQ-surfactant cooking shows behavior similar to that observed when adding wood lignin to the membrane system. Permeation is increased. Bulk reduction of AQ was also shown to be detrimental to AQ efficacy. Surface coverage and surface reaction are therefore the keys to enabling higher efficacy of AQ in pulping.

CHAPTER 6

PREDICTING PULPING RESULTS

The proposed mechanism for AQ mass transport into wood chips enables some amount of prediction for AQ efficacy based on the parameters of the cook. The model indicates that improved mass transfer results in improved pulping. From the mechanism, there are only two ways to enhance the mass transfer of AQ into the wood chips. By improving chip surface coverage of AQ and/or the reaction between AQ and carbohydrates (or other reducing agents inside the chip), the mass transfer can be increased. The "AQ uptake" mechanism also indicates that a longer time at low temperatures (100-120^{o}C) could also lead to improvements in pulping with AQ, as this gives time for AQ to begin concentrating in the chips.

Experimental

Pulping Operations

Pulping was conducted using the rotating multi-digester system at the Institute of Paper Science and Technology. Deionized water was used in all experiments. Eight pulping experiments were conducted in duplicate in a 2^{k} factorial experiment with three variables: rise time, initial AQ particle size, and initial reducing agent charge.

All cooks were soda-AQ cooks with effective alkali (EA) of 18% as Na2O, AQ charge of 0.1% on OD wood, and liquor to wood (L/W) ratio of 4:1. All cooks had a maximum cooking temperature of 170^{o}C, and they were quenched at an H-factor of 1800.

Treatments

High particle size AQ was standard AQ (Acros). For each cook with low particle size AQ, 0.1g of AQ powder was added to a small vial containing 5mL deionized water, 0.2g sodium dithionite (Aldrich) and 0.2g sodium hydroxide (Sigma). Once full reduction was accomplished (no visible particulates in the solution), the concentrated red solutions were then diluted and allowed to oxidize in air while stirred. The resulting milky suspension was then filtered, and washed with deionized water to remove the reaction products (sodium sulfite and sodium sulfate).

The chips were loblolly pine (*Pinus taeda L.*) wood either untreated or pretreated with glucose solution and allowed to air dry. The chips were approximately 59.1% carbohydrates and 30.4% lignin by weight. The pretreatment consisted of 10g D-glucose dissolved in 40mL deionized water. This was then added to the chips in a large beaker, and the beaker was covered and hand shaken to coat the chips. After air drying, the chips were again weighed, and the extra mass was subtracted from the total liquor weight to maintain the same L/W ratio.

Table 6.1: Conditions for pulping experiments

Experiment Number	Rise Time	AQ Particle Size	Chips Used
1	30 minutes	High	Untreated
2	90 minutes	High	Untreated
3	30 minutes	Low	Untreated
4	90 minutes	Low	Untreated
5	30 minutes	High	Pretreated
6	90 minutes	High	Pretreated
7	30 minutes	Low	Pretreated
8	90 minutes	Low	Pretreated

All cooks were conducted in a computer-controlled Aurora bomb digester system capable of six cooks per cycle. The resulting mass was pulverized in a blender (Waring) to fiberize the chips and washed with deionized water in a Buchner funnel with pre-weighed filter paper.

To determine total yield, the washed pulp was weighed, and samples of the pulps were dried to determine moisture content. The kappa number of the pulp was determined according to TAPPI method T236 om-6. Because yield and kappa number are not fully independent of each other, the lignin-free carbohydrate yield and carbohydrate-free lignin yield were calculated from the yield and kappa data.

Results and Discussion

Carbohydrate Yield

The effects of the variables on carbohydrate yield are presented in Table 6.2. Raw total yield and kappa number data are shown in Appendix A. It can be seen here that while the rise time and AQ particle size have a slight negative effect on carbohydrate yield, this effect is within experimental error. The addition of glucose has a significant impact on the carbohydrate yield. Carbohydrate yield was increased 2.67% by adding glucose to the wood chips. This may be due to the consumption of caustic by the additional glucose, decreasing the probability of endwise peeling and/or chain cleavage.

Contrary to this, there is a significant decrease in yield for the interaction effect of rise time and glucose addition. This is an indication that increasing the rise time in the presence of glucose will decrease the carbohydrate yield. This is shown graphically in Figure 6.1. The figure shows that when there is no glucose addition, increasing rise time works to increase the carbohydrate yield. However, in the presence of glucose, this is

reversed, and rise time decreases carbohydrate yield. This difference could account for the negligible effect seen in the individual effect.

Table 6.2: The individual and interaction effects of the variables on carbohydrate yield (%) and their probabilities of significance.

Source	Effect	Probability
Rise Time (A)	-0.176	18.5
AQ Part. Size (B)	-0.121	12.8
Chip Trtmnt. (C)	2.67	99.4
AB	-0.76	67.1
AC	-1.44	91.7
BC	-0.74	66.2
ABC	1.12	83.9

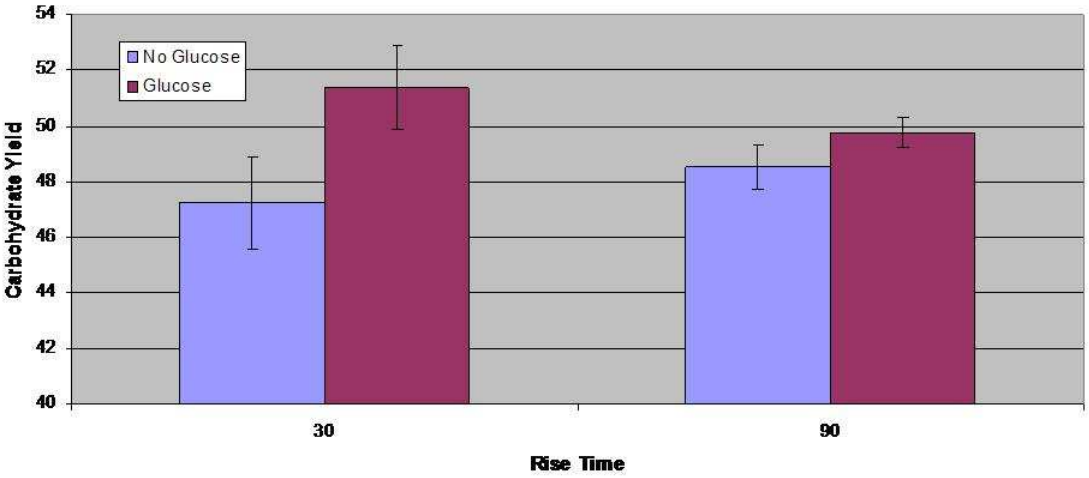

Figure 6.1: Means of carbohydrate yield (%) for different rise times and glucose contents. Error bars are 90% confidence interval.

Without glucose, the increased rise time is probably working according to the mechanism described previously. It is enabling the AQ to begin its diffusion process before reaching reaction temperature. In the presence of glucose, increased rise time is probably giving time for the bulk reduction of AQ as glucose is released from the surface

of the chip. This would result in a decreased diffusion of AQ into the chips, and reduced carbohydrate stabilization, leading to a reduced carbohydrate yield.

This interaction is similar to the interaction with glucose and AQ particle size. Though the interaction effect is significant only at the 66.2% confidence interval, the behavior is the same, as shown in Figure 6.2. Here, the particle size is reacting as it should in the absence of glucose, increasing the carbohydrate yield over the larger AQ. However, in the presence of glucose, the reduction in particle size only works to decrease the carbohydrate yield. In this case, the glucose is probably reacting in the bulk phase with the AQ once again. The increase in surface area from the reduction in particle size will make this reaction faster. This would lead to greater bulk reduction and a decrease in AQ diffusion, resulting in a decrease in carbohydrate yield. In this case, the reduction due to glucose and the increase due to particle size cancel each other out, making any changes non-significant

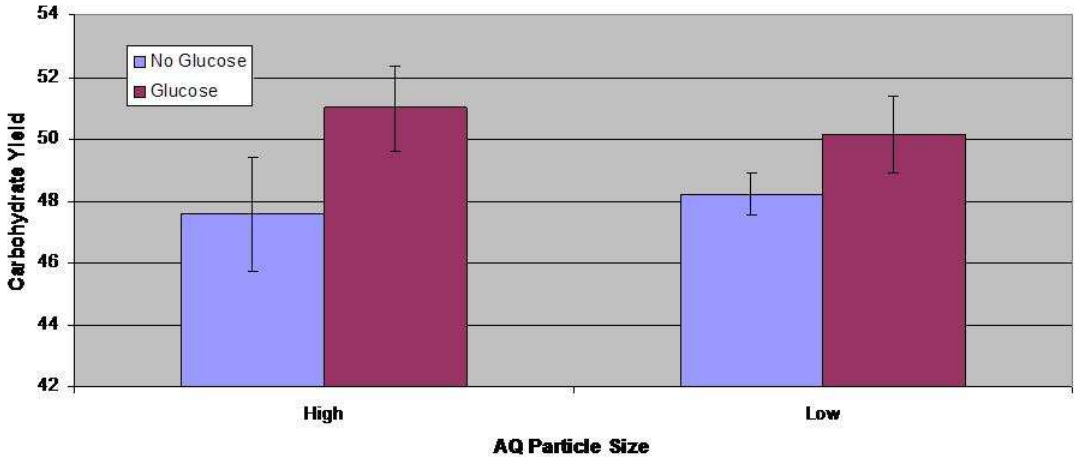

Figure 6.2: Means of carbohydrate yield (%) for different AQ particle sizes and glucose contents. Error bars are 90% confidence interval.

Lignin Yield

The effects of the variables on lignin yield are presented in Table 6.3. Here, all individual and interaction effects are significant at the 90% confidence interval, with the exception of the ABC interaction. In such a case only the interaction effects are important.

Table 6.3: The individual and interaction effects of the variables on lignin yield (%) and their probabilities of significance.

Source	Effect	Probability
Rise Time (A)	-0.422	95.2
AQ Part. Size (B)	-0.384	93.4
Chip Trtmnt. (C)	1.53	100.0
AB	-0.44	95.8
AC	-0.36	92.0
BC	-0.60	98.9
ABC	-0.05	19.9

In the absence of glucose, increased rise time causes a slight decrease in the lignin content of the pulp, as shown in Figure 6.3, though it is probably within experimental error. However, when glucose is added, the reduction in lignin content is pronounced. This simply could be due to the higher lignin content of the pulps from the treated chips. It has been shown previously that as cooks progress the impact of AQ is less noticeable [59]. This usually happens at higher H factors, probably due to the leveling off of delignification in the residual phase and consumption of AQ by side reactions. However, in this case all of the cooks contain AQ, so the differences from the changes in conditions may not be noticeable at this lower H factor. The large increase in lignin content due to the presence of glucose could enable viewing of this effect.

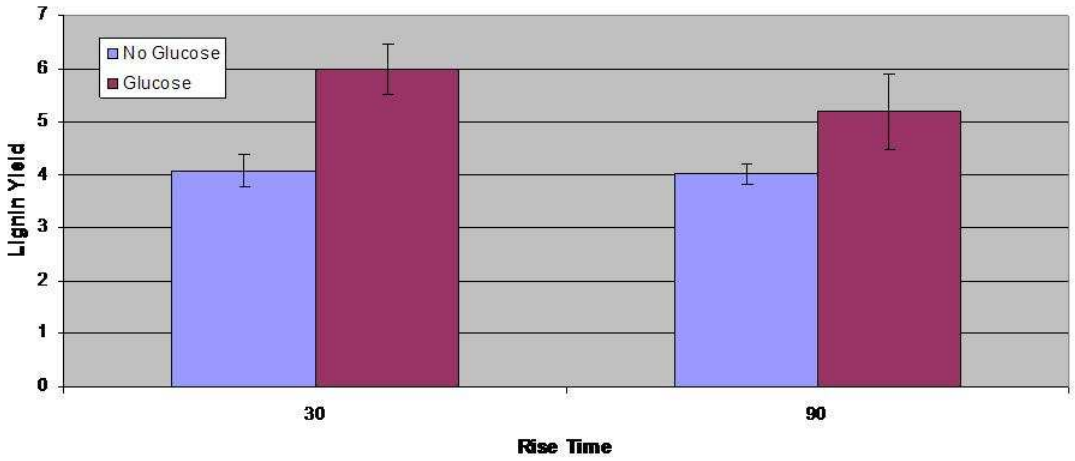

Figure 6.3: Means of lignin yield (%) for different rise times and glucose contents. Error bars are 90% confidence interval.

This may also explain the interaction between particle size and glucose. Here, decreasing the particle size slightly increases lignin yield, though this may again be within experimental error. Adding glucose once again makes the lignin content reduction evident, as it does for rise time.

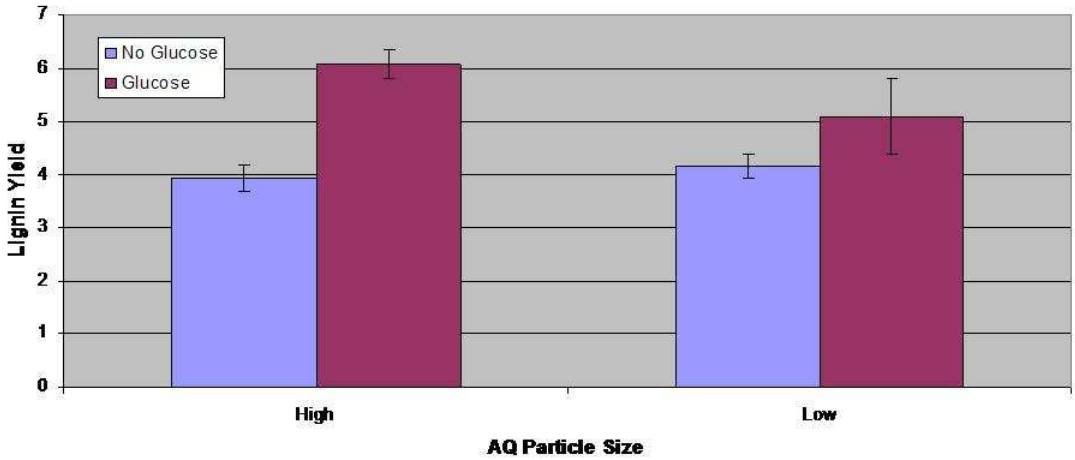

Figure 6.4: Means of lignin yield (%) for different particle sizes and glucose contents. Error bars are 90% confidence interval.

A very interesting interaction exists between particle size and rise time. Increased rise time has almost no effect with high particle size, but at low particle size, there is a significant reduction in lignin yield. This could be the result of the method of creating the low particle size AQ.

It was hoped that a scenario similar to that of AQ-surfactant pulping could be conducted in the absence of surfactant. When the AQ crystals reformed through oxidation, they may have incorporated some water into their crystal structure. This could decrease the hydrophobicity of the crystal, allowing it to stay suspended in the bulk liquor, rather than adsorbing to chip surfaces. Similarly, the reformed particles may have been small enough that the particles stayed suspended during the cook, similar to an emulsion. Either way, this would mean a reduction of chip surface coverage from what was expected due to an increase in external mass transfer resistance. There is not enough data to estimate the mass transfer Biot numbers for the reduced particle size AQ at this time. However, because of the very high external mass transfer coefficient discussed in Chapter 3, the change in hydrophobicity would have to be very large to have an impact on the external mass transfer.

The increased rise time could give the AQ a better chance to overcome the external mass transfer resistances that become more important with reduced hydrophobicity. This would increase surface contact and therefore diffusion, leading to a reduction in lignin content of the resulting pulp.

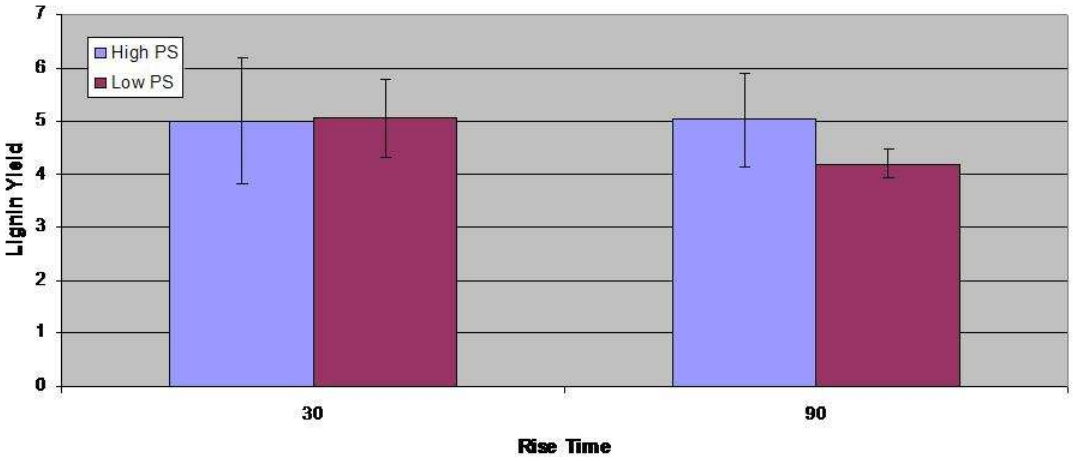

Figure 6.5: Means of lignin yield (%) for different rise times and particle sizes. Error bars are 90% confidence interval.

Relationship to Proposed Mechanism

The mechanism indicates that increased rise time, reduced particle size, and increased surface reduction should enhance mass transfer of AQ, and therefore the pulping selectivity. In this experiment, the first two of these where shown to be somewhat accurate. Both increased rise time and decreased particle size were shown to decrease the amount of lignin left in the pulp while maintaining the carbohydrate yield. However, there were some discrepancies. If glucose is removed from the experiment, there is no significant effect from either of these variables.

Table 6.4: Yield (%) data for cooks without glucose.

Source	Effect	Probability
Carbohydrate Yield		
Rise Time (A)	1.261	74.46
Particle Size (B)	0.621	45.06
AB	-1.879	88.07
Lignin Yield		
Rise Time (A)	-0.059	4.65
Particle Size (B)	0.216	16.86
AB	0.004	29.81

The extremely low probabilities for the lignin yield indicate that these factors have had no effect on delignification in the absence of glucose. This could be due to the aforementioned cooking time effect, or it may be due to the choices in procedure for these experiments. The problems with the low particle size have already been discussed.

The original intent of the rise time experiments was to examine more in depth the behavior of AQ with respect to rise time, as displayed in two previous articles. In one article, a very short rise time was produced by placing the digester in a preheated oil bath [55]. In the other, a more standard rise time was used [57]. Because of the limitations of the equipment used here, these conditions could not be reproduced. The low time chosen for this experiment was chosen so as not to damage the heating elements of the digester used. Too-rapid heating could cause the heaters to exceed their designed limits, thereby creating a hazardous situation. Even so, some of the heaters were not able to keep up with the programmed 30 minute rise time. On a couple of occasions, the rise time ended up closer to 40-45 minutes, instead of the programmed 30 minutes. This could lead to some discrepancies in the data. Also, the low time chosen in this experiment may be longer than a "critical time" at which the rise time has decreasing effect on pulping selectivity. Further experimentation should be conducted to determine if this is so, and what this "critical time" is should it be shown to exist.

Another possibility arises during the process of the cook itself. During the initial phase of cooking, many carbohydrates (hemicelluloses, starches, simple sugars, etc.) are leeched out from the chips. These then behave similarly to reduced species added to the bulk liquor – some of the AQ will be reduced in the bulk, rather than at the surface. This will affect any AQ cooks regardless of particle size. However, the lower particle size AQ

has a much higher surface area, and may therefore be more impacted by this than higher particle size AQ. This could then lead to a reduction in the effect from particle size.

Glucose

The addition of glucose to the surfaces of the chips has had a very significant, negative impact on selectivity. However, it did enable the viewing of the interaction effects. The problems observed in the use of glucose are most likely due to the method used for introducing the glucose to the chips.

The original intent of the experiment was to use glucose to enhance the surface reaction with AQ. More free glucose at the surface would allow more AHQ to form at the surface, and therefore enhance the rate at which AQ species enter the chip. It was assumed that the best way to do this was to increase the surface concentration of glucose. A very large amount of glucose was used expecting some losses.

Instead, putting this much glucose on the surface of the chip created an ideal place for the glucose to dissolve into the bulk liquor, thus creating a scenario similar to that presented in the previous chapter. It has already been shown that adding glucose to the system in the bulk liquor has a negative impact on pulping. The data obtained in these experiments add further proof to this.

Future experiments should be conducted to test the impact of increased reducing species inside the chip. For instance, if the glucose were allowed to permeate the chips instead of being on the surface, some of the bulk reduction effects can be avoided. One way to do this would be to create a larger, more dilute solution of glucose, and soak the chips in it for several hours. Allowing the chips to air dry after soaking will allow the glucose to remain, while driving out excess water. Then the dried chips could be rinsed

to remove any easily-dissolved glucose from the surface. A second air drying period would return the chips to the same state as before. These chips would not have as much problem with bulk reduction.

Concluding Statements

Of the three variables identified by the present model, only glucose did not act as indicated in the model. This may have been due to the method by which the glucose was added to the chips. Both increased rise time and decreased particle size decreased the amount of lignin in the pulp while maintaining the carbohydrate yield. They both increased pulping selectivity; however, the low probabilities of significance for these effects in the absence of glucose are worrisome. Future work should be conducted to better determine these effects, and to clear up the problems with applying glucose as in this method.

CHAPTER 7

CONCLUSIONS

By taking into account the works of many researches working with different aspects of AQ as well as behavior of AQ in a model system, a mechanism for the transport of AQ species into wood during alkaline pulping has been developed. Initial indications show that changing variables indicated by the mechanism can have a positive impact on the selectivity of pulping.

The mass transfer behavior of AQ in alkaline pulping may be more important than even the chemistry. This behavior is incredibly complex, as AQ is the only component in alkaline pulping that has shown the ability to exist inside the chip at a higher concentration than in the bulk liquor. It is demonstrated, therefore, that it is extremely important to study this behavior to learn to control this concentrating effect.

A model system has given some insight into the ways by which AQ permeates the wood chip. It was shown that the diffusion of reducing species from inside the membrane is responsible for the permeation of AHQ into the acceptor stream. The extent to which the surface of the membrane is coated by AQ can enhance the flux of AQ species across the membrane. It was also shown that bulk reduction in the donor solution can have a negative impact on the membrane permeation by AQ species.

The particle size and bulk reduction effects were then observed in pulping. It was shown that pulping selectivity can be improved through pulping with surfactants. The surfactants act to break up the AQ particles and cover more wood surface. It was also shown that AQ samples with higher specific surface can improve pulping. Bulk reduction can have a significant negative impact on the pulping selectivity. It was shown

that the addition of glucose to the white liquor greatly increased the residual lignin of a pulp. However, faster reducing species showed that bulk reduction could be beneficial if it is short-lived.

Finally, an initial pulping run based around these principles showed promise. It was shown that pulping selectivity could be slightly improved by increasing rise time and decreasing initial AQ particle size. All effects studied were inconclusive due to the size and nature of the experiment, but it shows promise as an early indication of pulping.

Future work should be conducted to more fully verify the actions of AQ in alkaline pulping. For instance, the pulping experiments could be conducted with a better application of glucose, as described previously. Likewise, steps could be taken to decrease the particle size of AQ without altering its hydrophobicity, such as grinding or milling, though this could lead to problems with agglomeration in the digester. Quantification of the diffusion coefficients and mass transfer resistances (both internal and external) in the model system and in pulping could also lead to the development of a mathematical model for the behavior of AQ in pulping. This would allow much greater understanding of the impact of mass transfer on the efficacy of AQ in pulping.

This work is a start, but there is much more yet to understand. With a better understanding of this complex mechanism, the full potential of anthraquinone in alkaline pulping can yet be unleashed.

APPENDIX A

COMPILED AQ PULPING DATA

Table A.1: Soda-AQ and Soda AQ modified cooks at # 5 digester.

Sample ID	Cook Temp (^{o}C)	H Factor	E.A. Added (%)	Residual E.A.(g/L)	Screen Yield (%)	Total Yield (%)	Kappa Number	Viscosity (cp)
#5095-10	160	1604	16	11.4	43.1	48.1	43.4	28.8
#5095-11	170	1631	16	12.6	39.4	46.9	50.1	22.0
#5095-17	170	1627	11.2 + 4.8	12.5	41.1	48.6	54.3	27.2
#5059-20	170	1622	18	14.4	41.0	44.4	39.0	18.5
#5059-28	170	1623	11.0 + 7.0	17.4	41.5	44.5	41.9	19.1

Pine chips 1000g (O.D. wt), AQ 0.1%, L:W 4, and ramp time 90 min.
For modified cook: L:W at start 3.5% and split E.A added at 160^{o}C (L:W 4 after addition).

Table A.2: Soda-AQ-Glucose cooks at 1 L 6 vessel rotating digesters. (The purpose of adding glucose in the middle of cook aims at enhancing AQ's redox cycle.)

Sample ID	Cook Temp (^{o}C)	H Factor	AQ Added (%)	Glucose Added (%)	Residual E.A.(g/L)	Total Yield (%)	Kappa Number	Viscosity (cp)
#5095-25-1	170	1000 + 600	0.1	0	18.4	46.9	34.1	21.4
#5095-25-2	170	1000 + 600	0.05 + 0.05	0	18.1	45.8	42.1	19.0
#5095-25-3	170	1000 + 600	0.05 + 0.05	1.0	17.7	46.0	41.0	22.9
#5095-25-4	170	1000 + 600	0.1	1.0	18.0	44.5	35.0	19.2

Pine chips 100g (O.D. wt), total E.A. 18%, AQ 0.1%, L:W 4, and ramp time 90 min. Glucose added in the middle of the cooks while H factor reached 1000. Some runs added the other half of AQ while H factor reached 1000. (When H factor reach 1000, the autoclaves were quenched in cool water, added glucose and the half AQ, and started ramp to 170^{o}C cooking temp again. Stopped while total H factor reached 1600.)

Table A.3: Soda-AQ –Sodium dithionite cooks at 1 L 6 vessel rotating digesters. (The purpose of adding sodium dithionite aims at enhancing AQ's redox cycle.)

Sample ID	Cook Temp (^{o}C)	H Factor	E.A. Added (%)	SDT Added (%)	Residual E.A.(g/L)	Total Yield (%)	Kappa Number	Viscosity (cp)
#5095-22-1	170	1600	18	0	17.8	44.6	34.9	19.5
#5095-22-2	170	1600	18	0.08 (AQ:SDT =1:1)	17.9	45.4	35.3	21.2
#5095-22-3	170	1600	18	0.32 (1:4)	17.8	46.0	34.2	20.8
#5095-22-4	170	1600	18	0.8 (1:10)	18.0	44.7	33.9	18.8
#5095-22-5	170	1600	18.58*	0.8 (1:10)	18.8	44.8	31.6	20.9

Pine chips 100g (O.D. wt), total E.A. 18%, AQ 0.1%, SDT (Sodium Dithionite) added basis on different mole ratios to AQ, L:W 4, and ramp time 90 min.

* Added 0.58% more NaOH, which assumed to be consumed by SDT.

Table A.4: Soda-AQ –Sodium dithionite/Glucose cooks at 1 L 6 vessel rotating digesters. (The purpose of adding sodium dithionite and glucose aims at enhancing AQ's redox cycle.)

Sample ID	E.A. Added (%)	AQ Added (%)	SDT Added (%)	Glucose Added (%)	Residual E.A.(g/L)	Total Yield (%)	Kappa Number	Viscosity (cp)
#5095-30-1	19.4*	0.1	2.0	0	20.9	43.9	30.0	20.8
#5095-30-2	19.4*	0.1	2.0	0	21.0	43.8	29.3	20.5
#5095-30-3	19.4	0	2.0	0	20.8	47.7	78.1	-
#5095-30-4	19.4	0	2.0	0	21.5	46.7	82.9	-
#5095-30-5	18	0.1	0	2.0	17.4	45.7	42.0	23.2
#5059-30-6	18	0.1	0	2.0	17.1	47.1	40.7	24.6

Pine chips 100g (O.D. wt), L:W 4, cook temp 170^{o}C, final H factor 1600, and ramp time 90 min.

* Based on 18% E.A., added 1.4% more E.A., which assumed to be consumed by SDT (sodium dithionate).

Table A.5: Table of pre-cook chip and bag weights.

Bag#	Bag Wt.	AD Chip Wt.	OD Chip Wt.	Total Treated Wt.	Treated Chip Wt.	Rise Time	Particle Size	Chip Treatment
1a	11.95	107.62	100.03	N/A	N/A	-1	-1	-1
1b	11.89	107.76	100.16	N/A	N/A	-1	-1	-1
2a	11.97	107.85	100.25	N/A	N/A	1	-1	-1
2b	11.93	107.73	100.14	N/A	N/A	1	-1	-1
3a	11.86	107.83	100.23	N/A	N/A	-1	1	-1
3b	11.96	107.65	100.06	N/A	N/A	-1	1	-1
4a	11.97	107.96	100.35	N/A	N/A	1	1	-1
4b	11.94	107.76	100.16	N/A	N/A	1	1	-1
5a	11.92	107.63	100.04	130.35	118.43	-1	-1	1
5b	11.95	107.74	100.14	130.10	118.15	-1	-1	1
6a	11.96	107.80	100.20	133.95	121.99	1	-1	1
6b	11.91	107.55	99.97	133.74	121.83	1	-1	1
7a	11.96	107.74	100.14	134.02	122.06	-1	1	1
7b	11.96	107.83	100.23	133.74	121.78	-1	1	1
8a	11.91	107.58	100.00	133.57	121.66	1	1	1
8b	11.88	107.57	99.99	133.42	121.54	1	1	1

Table A.6: Yield data factorial cooking experiment.

Bag#	Wet Filter	Total Wet Wt.	Wet Pulp Wt.	Consistency	Dry Pulp Wt.	% Yield
1a	25.32	378.46	341.19	14.07	48.01	48.0
1b	26.27	350.97	312.81	16.52	51.68	51.6
2a	27.63	405.93	366.33	14.69	53.80	53.7
2b	27.22	382.77	343.62	15.41	52.93	52.9
3a	26.30	363.88	325.72	16.40	53.42	53.3
3b	28.92	352.64	311.76	16.85	52.53	52.5
4a	25.97	351.52	313.58	16.83	52.78	52.6
4b	25.25	352.06	314.87	16.25	51.15	51.1
5a	24.54	367.34	330.88	18.14	60.02	60.0
5b	13.9	361.31	335.46	16.85	56.51	56.4
6a	11.54	361.43	337.93	16.57	56.00	55.9
6b	12.46	352.61	328.24	17.05	55.96	56.0
7a	13.57	372.97	347.44	16.02	55.64	55.6
7b	12.26	358.45	334.23	17.22	57.54	57.4
8a	12.14	360.00	335.95	15.90	53.40	53.4
8b	13.08	338.96	314.00	17.37	54.53	54.5

Table A.7: Kappa number data for factorial experiment.

Bag#	Wet Pulp	Consistency	Dry Pulp	Temperature	Correction	Thiosulfate	p	C	f#	Kappa
1a	0.544	91.92	0.500	23	1.026	23.4	24.7	49.4	0.999	50.6
1b	0.544	92.06	0.501	23	1.026	23.5	24.6	49.2	0.998	50.3
2a	0.551	90.91	0.501	23	1.026	21.8	26.3	52.6	1.005	54.1
2b	0.551	90.98	0.501	24	1.013	23.3	24.7	49.4	0.999	49.9
3a	0.548	91.18	0.500	24	1.013	21.9	26.1	52.2	1.004	53.1
3b	0.569	87.85	0.500	24	1.013	20.2	27.8	55.6	1.01	56.9
4a	0.55	91.05	0.501	24	1.013	23.3	24.7	49.4	0.999	49.9
4b	0.548	91.12	0.499	24	1.013	22.7	25.3	50.6	1.001	51.4
5a	0.454	92.13	0.418	23	1.026	18.3	28.7	57.4	1.016	71.5
5b	0.366	91.19	0.334	24	1.013	23.7	23.3	46.6	0.993	70.2
6a	0.449	93.22	0.419	23	1.026	19	28	56	1.013	69.5
6b	0.449	92.86	0.417	24	1.013	18.5	29.5	59	1.015	72.7
7a	0.456	92.92	0.424	23	1.026	17.5	30.5	61	1.024	75.6
7b	0.365	93.18	0.340	23	1.026	27.5	20.5	41	0.981	60.7
8a	0.448	93.83	0.420	23	1.026	24	24	48	0.996	58.3
8b	0.466	92.96	0.433	22	1.039	25.3	21.7	43.4	0.986	51.3

Table A.8: Repeat kappa number data for factorial experiment.

Bag#	Wet Pulp	Consistency	Dry Pulp	Temperature	Correction	Thiosulfate	p	C	f#	Kappa
1a	0.542	91.93	0.498	23	1.026	23.5	24.6	49.2	0.998	50.6
1b	0.544	92.06	0.501	23	1.026	23.2	24.9	49.8	1	51.0
2a	0.550	90.91	0.500	24	1.013	21.4	26.7	53.4	1.007	54.5
2b	0.549	90.98	0.499	24	1.013	24.5	23.5	47	0.994	47.4
3a	0.548	91.18	0.500	24	1.013	21.3	26.7	53.4	1.007	54.5
3b	0.569	87.85	0.500	24	1.013	20.3	27.7	55.4	1.01	56.7
4a	0.548	91.05	0.499	24	1.013	23.5	24.5	49	0.998	49.6
4b	0.549	91.12	0.500	24	1.013	22.5	25.5	51	1.002	51.7
5a	0.452	92.13	0.416	23	1.026	17.6	29.4	58.8	1.019	73.8
5b	0.376	91.19	0.343	24	1.013	23.3	23.7	47.4	0.995	69.7
6a	0.459	93.22	0.428	24	1.013	18.5	28.5	57	1.015	68.5
6b	0.446	92.86	0.414	23	1.026	18.4	28.6	57.2	1.015	71.9
7a	0.451	92.92	0.419	23	1.026	18.1	29.9	59.8	1.021	74.7
7b	0.371	93.18	0.346	23	1.026	27.4	20.6	41.2	0.981	60.0
8a	0.472	93.83	0.443	22	1.039	23.6	24.4	48.8	0.998	57.1
8b	0.465	92.96	0.432	22	1.039	25.4	22.6	45.2	0.989	53.7

Table A.9: Yates' algorithm and ANOVA table for carbohydrate yield data.

Trmt. Comb.	Result	(1)	(2)	(3)	Effect	SS
1	92.0	190.3	383.1	787.6		
a	98.3	192.8	404.5	-1.4	-0.176	0.1243
b	97.0	204.0	5.0	-1.0	-0.121	0.0583
ab	95.8	200.5	-6.5	-6.1	-0.756	2.2889
c	104.0	6.3	2.5	21.4	2.672	28.5521
ac	100.0	-1.2	-3.4	-11.5	-1.437	8.2624
bc	101.5	-4.0	-7.5	-5.9	-0.742	2.1996
abc	99.0	-2.5	1.5	9.0	1.123	5.0425

Source	DF	SS	MS	F	$F_{1,8,0.1}$
Rise Time (A)	1	0.1	0.1	0.1	3.46
AQ Part. Size (B)	1	0.1	0.1	0.0	3.46
Chip Trtmnt. (C)	1	28.6	28.6	13.5	3.46
AB	1	2.3	2.3	1.1	3.46
AC	1	8.3	8.3	3.9	3.46
BC	1	2.2	2.2	1.0	3.46
ABC	1	5.0	5.0	2.4	3.46
Error	8	16.9	2.1		
Total	15	63.44125			

Error SS = Total SS - S(Effect SS)

Total SS = $S(y^2) - (Sy)^2/n$

F = Effect MS/Error MS

Table A.10: Yates' algorithm and ANOVA table for lignin yield data.

Trmt. Comb.	Result	(1)	(2)	(3)	Effect	SS
1	7.6	15.8	32.4	77.1		
a	8.2	16.7	44.7	-3.4	-0.422	0.7111
b	8.8	24.3	-0.2	-3.1	-0.384	0.5897
ab	7.9	20.4	-3.1	-3.5	-0.438	0.7686
c	12.5	0.7	0.9	12.3	1.532	9.3878
ac	11.9	-0.9	-3.9	-2.9	-0.363	0.5260
bc	11.5	-0.6	-1.6	-4.8	-0.600	1.4400
abc	8.9	-2.5	-1.9	-0.4	-0.047	0.0089

Source	DF	SS	MS	F	$F_{1,8,0.1}$
Rise Time (A)	1	0.7	0.7	5.4	3.46
AQ Part. Size (B)	1	0.6	0.6	4.5	3.46
Chip Trtmnt. (C)	1	9.4	9.4	71.8	3.46
AB	1	0.8	0.8	5.9	3.46
AC	1	0.5	0.5	4.0	3.46
BC	1	1.4	1.4	11.0	3.46
ABC	1	0.0	0.0	0.1	3.46
Error	8	1.0	0.1		
Total	15	14.477951			

Error SS = Total SS - S(Effect SS)

Total SS = $S(y^2) - (Sy)^2/n$

F = Effect MS/Error MS

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